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Ⓢ Supporting Information

ABSTRACT: This paper describes physical-organic studies of charge transport by tunneling through self-assembled monolayers (SAMs), based on systematic variations of the structure of the molecules constituting the SAM. Replacing a −CH₂CH₂− group with a −CONH− group changes the dipole moment and polarizability of a portion of the molecule and has, in principle, the potential to change the rate of charge transport through the SAM. In practice, this substitution produces no significant change in the rate of charge transport across junctions of the structure Ag^{TS}-S(CH₂)$_m$X(CH₂)$_n$H//Ga$_2$O$_3$/EGaIn (TS = template stripped, X = −CH₂CH₂− or −CONH−, and EGaIn = eutectic alloy of gallium and indium). Incorporation of the amide group does, however, increase the yields of working (non-shorting) junctions (when compared to n-alkanethiolates of the same length). These results suggest that synthetic schemes that combine a thiol group on one end of a molecule with a group, R, to be tested, on the other (e.g., HS∼CONH∼R) using an amide-based coupling provide practical routes to molecules useful in studies of molecular electronics.
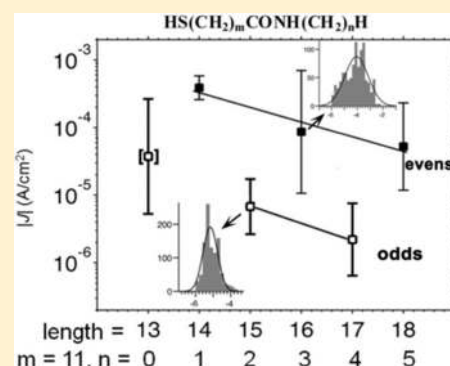
INTRODUCTION

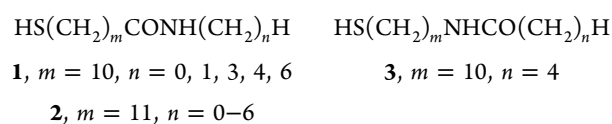Understanding charge transport through organic molecules and supramolecular structures is important in fields from biology[1−5] to materials science.[6−18] In biology, understanding the flow of electrons in redox biochemistry requires understanding the relation between molecular structure and rates of charge transport. In materials science, it is important in evaluating the potential of tunneling devices based on organic matter for use in electronics: the concept of "wave function engineering"—that is, designing and shaping tunneling barriers by molecular design—has been an influential and theoretically attractive, but practically unproven, starting point for a number of concepts proposed for molecular electronics.

We,[19−23] and others,[24−47] are developing experimental systems for investigating charge transport by tunneling across self-assembled monolayers (SAMs) as a function of the structure of the molecules making up the SAMs. An ideal system would offer (i) convenience and reproducibility, (ii) robustness (i.e., the ability to generate statistically significant numbers of data rapidly), and (iii) versatility (i.e., the ability to modify, easily and rapidly, the structure of the organic part of the junction through synthesis). This paper describes the measurement of current density (J, amps/cm²), as a function of applied bias (V), in molecular junctions comprising self-assembled monolayers (SAMs) formed from thiols having the

structure **1**, **2**, or **3**, adsorbed on so-called "ultra-flat", template-stripped silver (Ag^{TS}) substrates, and contacted by cone-shaped

HS(CH₂)$_m$CONH(CH₂)$_n$H   HS(CH₂)$_m$NHCO(CH₂)$_n$H

1, $m = 10$, $n = 0, 1, 3, 4, 6$ **3**, $m = 10$, $n = 4$

2, $m = 11$, $n = 0−6$

top-electrodes of the liquid eutectic of gallium and indium with its surface film of native oxide (Ga$_2$O$_3$/EGaIn).[19,21−23,48] The junctions described in this paper are similar to the Ag^{TS}-S(CH₂)$_n$H//Ga$_2$O$_3$/EGaIn junctions that we have described previously,[23] except for the substitution of −CONH− groups for −CH₂CH₂− groups.

This project had two objectives. (i) We wished to make a controlled perturbation to the structure of the n-alkanethiolates (which have been the predominant subject of studies of processes involving SAMs), and to determine the influence of this perturbation on the rates of charge transport across these SAMs. The amide group (−CONH−) is one of the best understood in organic chemistry,[49,50] and while not isostructural with −CH₂CH₂− is similar in size, and is known, from prior

work, to be compatible with the formation of SAMs.[51−55] (ii) Perhaps more importantly, we wished to develop a system of SAMs to use in studies of charge transport that was more easily modified structurally than are derivatives of *n*-alkanethiolates. Preparing compounds of the structure $HS(CH_2)_nR$, where *n* = 10−20, and R is a group that we might wish to select, with as few restrictions as possible, from the full range of organic and organometallic groups, can be synthetically arduous. By comparison, compounds of the structure $HS(CH_2)_{\sim 10}CONH$-$(CH_2)_nR$ are relatively simple to make, since amide-forming reactions are among the most versatile in organic synthesis in their ability to couple different groups. We knew—from other work—that amide groups are compatible with SAMs, and that the literature contains data suggesting that they are more stable (perhaps because of interchain hydrogen bonding) than are simple *n*-alkanethiolate-containing SAMs.[51−55]

Examination of current as a function of voltage for these amide-containing SAMs yielded two important results: (i) substituting an amide moiety, −CONH−, for an ethylene moiety, −CH_2CH_2−, resulted in no significant change in current density, and (ii) introducing the amide group into the SAM raised the yield of non-shorting junctions from ∼80−90%[23] to ∼100%. The former results indicate that even a large (from the vantage of organic chemistry) change in the electronic structure, dipole moments, and other properties of the SAM does not significantly influence the rate of charge transport by tunneling. It also provides a reality check on the idea that "wave function engineering" may provide an easy method of designing new materials with currently unprecedented charge-transport properties. The latter result suggests that amides (and perhaps other functional groups capable of interchain hydrogen bonding) may provide the structural basis for a useful strategy to use in improving the robustness and practicality of SAM-based tunneling junctions and other devices.

This project is complementary to a related study using the same type of junction.[56] In this other study, we used SAMs made up of a related structure (**4**), also containing an amide group. The objective of work involving **4** was different from

$$HS(CH_2)_4CONHCH_2CH_2R$$

4

that in this paper. It was designed to examine the influence of the structure of the R group (chosen to include a number of different aliphatic and aromatic groups) on the tunneling current for SAMs of approximate constant thickness. It also compared the amide-containing compounds with homologous *n*-alkyl thiolates of the same length, and concluded that both compounds tunnel currents at almost similar rates (any difference was less than a factor of 3).

■ BACKGROUND

Charge Transport in Insulating Organic Molecules. The current consensus in the field of molecular electronics is that charge transport in SAMs of insulating organic molecules proceeds via non-resonant, through-bond tunneling.[20,23,34,42,57−64] This behavior is typically modeled by a simple form of the Simmons equation (eq 1).[65]

$$J = J_0 e^{-\beta d} \tag{1}$$

In this equation, J (A/cm^2) is the current density flowing between the electrodes, d is the length of the molecule (in either Å or number of non-hydrogen atoms in the extended chain, n), J_0 is the current density in the hypothetical case of a junction with a SAM of zero thickness, but still including the contribution of all interfaces in the junction, and β (either Å^{-1} or per number of non-hydrogen atoms, n^{-1}) is an attenuation factor related to the shape and height of the tunneling barrier posed by the SAM.

We[19,21−23] and others[66−68] have previously reported that J through SAMs of *n*-alkanethiols is approximately log-normally distributed (albeit often with long, asymmetrical tails and significant outliers), rather than normally distributed, and have suggested that variations from junction to junction in thickness and in the number or type of defects in the SAM and electrodes would lead to a normal distribution in the effective thickness, d, of the SAM.[19,21−23,66,69] Since J is exponentially dependent on a normally distributed parameter (eq 1), J itself should be log-normally distributed.

We have reviewed the literature on charge transport through SAMs of alkanethiols, and found a consensus for the value of β = 0.8−0.9 Å^{-1} (1.0−1.15 n_C^{-1}) across many techniques;[70] we also found a much looser consensus for a value of J_0 ($J_0 \approx 10$−10^3 A/cm^2) in junctions of the form metal-SAM//(protective layer)/liquid metal. (We discuss the significance of the "protective layer" in another paper.[48])

We have demonstrated a statistically significant difference in J between alkanethiols with odd and even numbers of carbon atoms (the so-called "odd−even" effect).[23] Specifically, J for odd-numbered alkanethiols is roughly 1 order of magnitude smaller than what one would predict for the same thickness from an interpolation of J for even-numbered alkanethiols. In this work, we infer that this "odd−even" effect persists in SAMs containing amide moieties.

Properties of Alkanethiol SAMs Compared to SAMs Containing Secondary Amides. It has been repeatedly demonstrated that the strong metal−sulfur bond (168 kJ/mol) and the favorable van der Waals interactions,[71−73] supplemented by interchain hydrogen bonds, restrict conformational mobility of the alkyl chains in SAMs containing secondary amides, and generate an ordered assembly in these monolayers.[51−55,74−76] Incorporating interchain hydrogen bonds in SAMs decreases the density of defects, and increases thermal stabilities of amide-containing SAMs, compared to SAMs of *n*-alkanethiols.[51−53,55,75,77,78] In the current study we replaced ethylene units, −CH_2CH_2−, in alkanethiols with secondary amide moieties, −CONH− or −NHCO−, where both orientations of the amide moiety are capable of interchain hydrogen-bonding.[79]

■ EXPERIMENTAL DESIGN

SAMs Containing Secondary Amides. Amides are important functional groups throughout organic chemistry.[49,50,79] From a practical point, amides are readily synthesized,[2,8] and can be used to introduce, or couple, many functional groups into a molecular system.

Why Secondary (−CONHR−) Amides? This work focuses on secondary amides because (i) they have the potential to form intermolecular hydrogen bonds when incorporated into a SAM; (ii) the absence of a second *N*-alkyl group leads to less interference with self-assembly than would more hindered structures such as −CON-(R')R, and therefore the charge transport characteristics of SAMs incorporating −CONH− groups can be compared to those of *n*-alkanethiolate SAMs (which are often seen as a baseline/standard system); and (iii) although a −CONH− group has only small

structural/steric differences from a $-CH_2CH_2-$ group, amides have a large ($\mu \approx 4$ D)[80−84] group dipole moment. Tertiary amides, are sterically larger than $-CH_2CH_2-$ groups, and cannot be directly compared to n-alkanethiols. Primary amides place a polar $-CONH_2$ group at the interface with the Ga_2O_3 film, and as such can perhaps not be directly compared with n-alkanethiolates.

Position of the Amide. We synthesized thiols, HS-$(CH_2)_mCONH(CH_2)_nH$, with the amide moiety separated from the thiol group by 10 or 11 methylene units ($m = 10$ or 11). We chose a C_{10} or C_{11} spacer to allow for a well-ordered region between the amide moiety and the thiol.[73,85]

Use of n-Alkanethiolate SAMs as Bracketing Standards. Data were collected over long intervals of time (days to months apart), and random and/or systematic errors (environmental and seasonal variations, differences among operators, changes in equipment) were probably unavoidable. To make sure that data collected at different times by different operators were comparable, we used two n-alkanethiols (octadecanethiol and dodecanethiol) that bracket the values of J(V) of interest in this work to calibrate values obtained with new compounds or from multiple users; we call these thiols (C_{12} and C_{18}) "bracketing standards". We took measurements of these two SAMs periodically during collection of data on amide-containing SAMs, and compared these data to those previously reported[21,23] using the EGaIn/Ga_2O_3 top electrode. Measurements using the standards were collected randomly throughout the study, with the first 3−5 tunneling junctions measured in any set of experiments being from the two standards, before starting to measure the amides. Whenever the measured standards deviated from the literature by more than an order of magnitude, the experiment was stopped, a new tip formed, and data re-collected. By applying a randomized system of measuring the standards, we minimized uncontrolled variations in the measurements.

Management of Measurement Variability. To minimize and manage experimental errors, we have developed a standard operating procedure and well-defined statistical tools for this work.[69] We collected data generated by multiple users, to avoid a single-user bias in the results. We pooled all non-shorting (working junctions only) data from different users, and summarized the pooled data as histograms. To these histograms, we fitted Gaussian curves using a non-weighting algorithm to avoid biasing the data due to outliers.[69]

Statistical Analysis of log($|J|$) Rather Than J. As noted previously by us[22,23] and others,[43,66,67,86] J is log-normally distributed, rather than normally distributed—that is, log($|J|$) is (approximately) normally distributed. We chose, therefore, to plot and fit histograms of log($|J|$), rather than J. When necessary, we used two-sample t tests[69] to determine whether the distributions of log($|J|$) for two compounds had distinguishable or indistinguishable means, at the 99% confidence level. Since the t test assumes normality, and since the distributions we observe sometimes deviate from normality, the statistical inferences from t tests are suggestive but not conclusive.

■ RESULTS AND DISCUSSION

Synthesis of Amides. Scheme 1 summarizes the general procedure—two consecutive two-step reactions—we used to synthesize all molecules (see Supporting Information for details). Synthesis followed by chromatographic purification gave the target thiols in 45−81% yields over four steps, and in high purity (as determined by ^{1}H NMR). As previously discussed,[23] we purified the thiols carefully, by column chromatography using 15% ethyl acetate in n-hexanes as eluant, before forming SAMs. The purified thiols were stored under N_2 and refrigerated when necessary. When, or if, the molecules degraded, they were re-purified by column chromatography, and purity was confirmed by ^{1}H NMR. For convenience, we abbreviated the names of the compounds using the assignments in Table 1. For each compound investigated, we measured between 10 and 52 junctions—individual points of contact between a Ga_2O_3/EGaIn tip and the SAM—and collected

Scheme 1. Synthesis of Mercapto-N-alkylamides ($m = 10$ or 11) from the Respective Primary Bromocarboxylic Acid via a Bromoalkylamide[a]
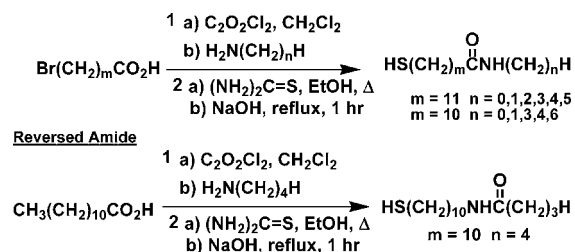
[a]Subsequent reaction with thiourea followed by hydrolytic cleavage of the resulting isothiuronium salt gave the target thiol. The reverse amide was synthesized in a similar manner. The thiols were obtained in 45−81% yield over the four steps.

Table 1. Junction Performance Results for Measurements on Mercapto-N-alkyl Amides of the Form $S(CH_2)_mCONH(CH_2)_nH$, Abbreviated as m,n, and of the Form $S(CH_2)_mNHCO(CH_2)_nH$, Abbreviated as m,n*

compd	no. of Ag^{TS} substrates	junctions[a]	N	failed junctions[b]	yield (%)
[11,0]	1	23	780	1	[96][c]
11,1	3	52	2144	0	100
11,2	1	24	1008	0	100
11,3	2	24	974	1	96
11,4	1	10	420	0	100
11,5	2	51	1782	0	100
[10,0]	1	28	1176	0	[100][c]
10,1	1	26	1026	0	100
10,3	1	19	758	0	100
10,4	1	12	466	0	100
10,6	1	18	768	0	100
10,4*	1	15	604	1	93

[a]Includes all junctions, both working and failed. [b]Failure was identified by current that reached the compliance limit of the electrometer (105 mA): the equivalent to a short circuit. [c]Square brackets, [ ], indicate a terminal primary amide; these compounds may not be comparable to the $-CH_3$ terminated ($n = 1−6$) compounds.

roughly 20 J(V) traces for each junction. A J(V) trace involved sweeping from 0 V → +0.5 V → −0.5 V → 0 V in steps of 50 mV, with a delay of 0.2 s between each step in applied bias, while measuring J at each bias. Thus, one J(V) trace yielded two values of J for each value of applied bias. Using this protocol, we collected between 400 and 2200 values (N) of J at every applied bias for each molecule. Collecting data for each compound required between 2 and 12 h (depending on N); in some cases, measurements were spread out over multiple (sometimes non-consecutive) days, although data collected over short periods of time had fewer variations and gave more tightly clustered data. Before collecting data for a particular amide-containing SAM, we measured current densities across each of the two bracketing standards from 3−5 junctions, and then randomly repeated throughout the analysis after every 10 junctions.

Yield of Junctions Incorporating SAMs with Internal Amides. For the series of secondary amides with $m = 10$ or 11, we observed only two shorting junctions out of 287 ($N = 11$ 302) total junctions measured (99% yield, Table 1). By contrast, the yields of working junctions incorporating SAMs of n-alkanethiols ($S(CH_2)_{n−1}CH_3$, $n = 9−18$) averaged ~80−

90%.[23] We attribute the high yields of junctions derived from amide-containing SAMs to the formation of a network of intermolecular hydrogen bonds extending across the SAM.[51−53,55,74,77,87−90]

Estimates of β and J_0 for Alkyl Amides. For these amide-containing SAMs, we do not have data over a sufficiently broad range of lengths to generate confident estimates of β and J_0 by fitting $\langle \log |J| \rangle$ vs n to the Simmons equation.[91] We exclude from our analysis compounds **10,0** and **11,0**, since they terminate in a $-CONH_2$ group rather than a $-CH_3$ group. We draw three qualitative conclusions from the data. (i) Within the uncertainty of the measurements, it is not possible to distinguish between n-alkanethiolates and amides with the same length (Figure 1). This statement is not the same as an assertion that there *is* no difference, only that within the uncertainties of these measurements ($\leq \pm 1$ unit in $\log |J|$), we cannot distinguish them. (ii) It appears that the difference between chains with odd and even numbers of atoms in the backbone of the chain, observed previously,[23] is still preserved
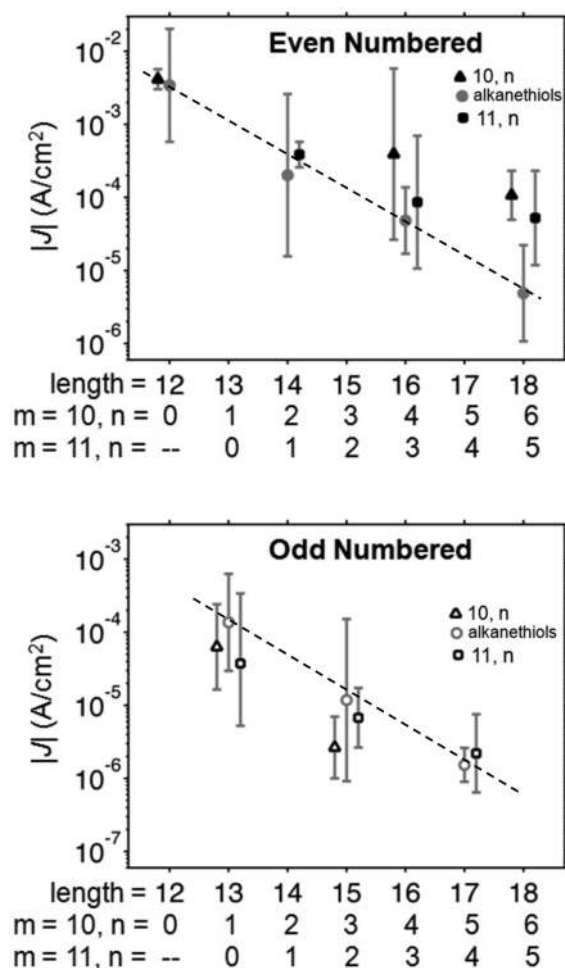

Figure 1. Plot of $\langle \log |J| \rangle$, at $V = -0.5$ V, vs the number of atoms in the molecular backbone for three types of SAMs: triangles, **10,n**, amides n = 0, 1, 3, 4, 6; squares, **11,n**, amides $n = 0−5$); and circles, **11,n**, n-alkanethiols $n = 12−18$). Closed symbols (top panel) represent compounds with an even length (in terms of the number of non-hydrogen atoms in the molecular backbone), while open symbols (bottom panel) represent compounds with an odd length. The dashed line highlights the best linear fit for the n-alkanethiols and is given as a guideline, and as an aid in comparing the behavior of the amides.

in the amides (Figure 2). A crude estimate of the difference between values of $\langle \log |J| \rangle$ for a hypothetical, common,
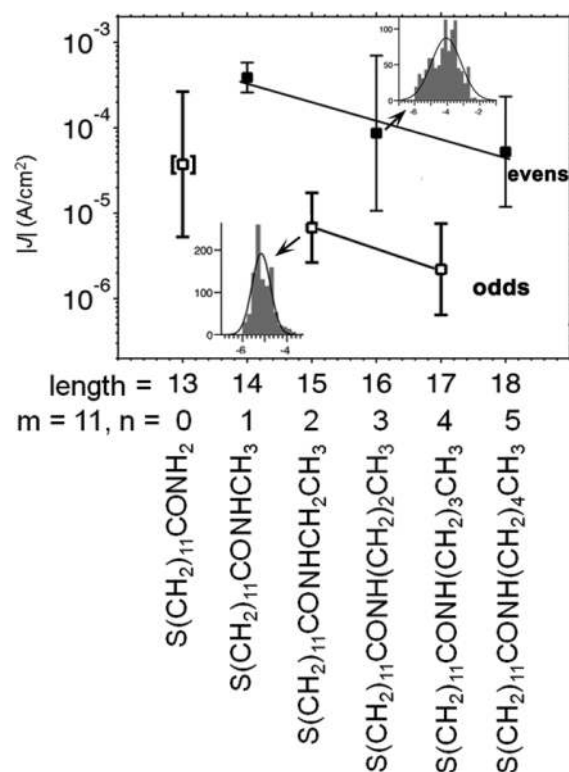

Figure 2. Plot of $\langle |J| \rangle$, at $V = -0.5$ V, vs the total length of the molecule (i.e., the number of bonds in the longest *trans*-extended chain) for alkyl amides with $m = 11$. All molecules with an even length (filled squares) gave higher current densities than those having an odd length (open squares). The two inserts are histograms of $\log |J|$, plotted against counts, for **11,2** and **11,3** compounds to illustrate the relationship between the standard deviation in the data and the spread in the histograms of the data. The structures of the different molecules are given below the x-axis. The primary amide, **11,0**, is marked with square brackets, [ ], as a reminder that this interface is different from the other $-CH_3$ terminated compounds and as such, perhaps, cannot be compared directly. The two lines are inserted to highlight how the molecules segregate into two groups of "odd" and "even" lengths.

extrapolated length suggests that for these amides, the value of $\langle \log |J| \rangle$ is higher by by a factor of ~ 1 (with an unquantified uncertainty) for the even-numbered compounds than for the odds (albeit from fitting only five data); for comparison, the value of $\langle \log |J| \rangle$ previously estimated from more precise data for n-alkanethiolates, the evens are higher than the odds by a factor of ~ 1. (iii) The small number of data do not support a useful estimate of β. If, however, we constrain the amide $|J_{0,even}|$ to have a value similar to that estimated for the n-alkanethiols ($J_{0,even} \approx 5.4 \times 10^2$ A/cm^2),[23] since the values for J for amide-containing and n-alkyl thiolates SAMs are indistinguishable, then the values for β must be similar (we calculated $\beta_{even} \approx 1.0$ n^{-1}, where n is the total number of non-hydrogen atoms in the trans-extended form of the amides).

Substituting an Amide for an Ethylene Unit Has No Discernible Effect on σ_{log}. We also compared the log-standard deviation, σ_{log}, of data derived from amides to those derived from n-alkanethiols (Table 2). We observed no consistent difference in σ_{log} between the two classes of compounds. This result tentatively suggests that the main

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Table 2. Comparison of Log-Means, $\langle \log |J| \rangle$, and Log-Standard Deviations, σ_{log}, for SAMs Derived from the Amides with Those from n-Alkanethiols of Analogous Lengths

compd	$\langle \log |J| \rangle \pm \sigma_{log}$	
	amides	$S(CH_2)_nH$
11,0	-4.4 ± 0.9	-3.9 ± 0.7
11,1	-3.4 ± 0.2	-3.7 ± 1.1
11,2	-5.2 ± 0.4	-4.9 ± 1.1
11,3	-4.1 ± 0.9	-4.3 ± 0.5
11,4	-5.7 ± 0.5	-5.8 ± 0.2
11,5	-4.3 ± 0.7	-5.3 ± 0.7
10,0	-2.4 ± 0.1	-2.5 ± 0.8
10,1	-4.2 ± 0.6	-3.9 ± 0.7
10,3	-5.6 ± 0.4	-4.9 ± 1.1
10,4	-3.4 ± 1.2	-4.3 ± 0.5
11,6	-4.0 ± 0.3	-5.3 ± 0.7

advantages of having an internal amide—high yields of working junctions and ease and flexibility in synthesis—comes without a trade-off in the spread of $\log(|J|)$.

Reversing the Orientation of the Amide, $-CONH-$ vs $-NHCO-$, Does Not Make a Significant Difference to Either $\langle \log |J| \rangle$ or σ. We synthesized and measured one compound with the amide moiety reversed [**10,4***, S-$(CH_2)_{10}NHCO(CH_2)_3CH_3$]. Figure 3 compares the histograms of **10,4*** and **10,4**. Reversing the orientation of the amide moiety lowered the mean value of $\langle \log |J| \rangle$ by 0.6 log unit $(\Delta J = 10^{0.6}$ A/cm^2), but this difference is not statistically significant ($p > 0.1$), and the two values are not distinguishable.
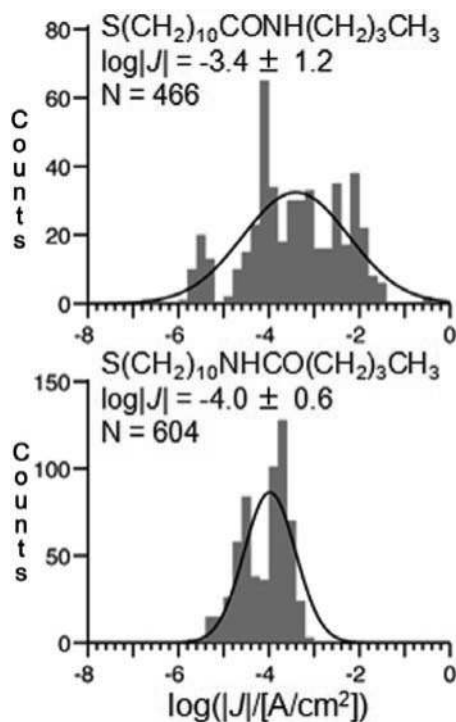

Figure 3. Histograms of log |J| for two alkyl amides, **10,4** and **10,4***, compounds in which the orientation of the amide has been reversed but the total length of the molecule is the same. The spreads in the distributions for the two compounds overlap, making the averages of log |J| indistinguishable.

Junctions with Structure Ag^{TS}-SAM//Ga$_2$O$_3$/EGaIn, Based on SAMs with Amides, Do Not Rectify. Aviram and Ratner proposed,[92] and others have claimed,[93−101] that diode-like rectification of current can result from two accessible molecular orbitals—an electron acceptor and an electron donor—arranged in series along the path of charge transport. We have shown a simpler way of achieving rectification than the Aviram−Ratner approach: placing a single accessible molecular orbital asymmetrically between two electrodes (i.e., at the terminus of an alkanethiol chain).[21,22] Others have proposed that even an accessible molecular orbital is not required—that a dipole with a component along the axis of charge transport is sufficient to cause rectification by "tilting" the tunneling barrier and breaking the symmetry between the wave functions of electrons approaching the barrier from the left and right.[101] An amide has a large dipole moment ($\mu \approx 4$ D).[81,83,84] Placing an amide within the SAM does not produce an easily quantifiable change in that component of the dipole moment that might be relevant to the shape of the tunneling barrier for a number of reasons (the orientation of the dipole, partial cancellation of dipoles on adjacent molecules, and uncertainties concerning the path of the electron during tunneling, among others). Nonetheless, it seemed worthwhile to test our set of amide-containing SAMs for rectification. We calculated the raw rectification ratio, r, as the ratio of the current density at opposing values of applied bias,

$$r = J(+V)/J(-V) \qquad (2)$$

For all molecules synthesized, we calculated the value of r, at $V = \pm 0.5$ V, for each trace, plotted values of log |r| in histograms (r, like J, is log-normally distributed), and fitted Gaussians to the histograms to determine the mean and standard deviation of log |r|. All of the amides gave values of log |r| that were close to zero, and similar to those of n-alkanethiols in magnitude and polarity (Table 3). Figure 4 and Table 3 illustrates that there was no significant effect of position (varied by one carbon) and/or structure on the rectification ratio. The small rectification at positive bias observed with these amide molecules is comparable to that observed with n-alkanethiolate SAMs (Table 3, column 6) and could arise from

Table 3. Rectification Ratios Observed for All Amides Containing SAMs in an Ag^{TS}-SAM//Ga$_2$O$_3$/EGaIn^a

amide[b]	N_J	$\langle \log |J| \rangle$	σ	$|+r|^c$	
				amides	$S(CH_2)_nH$
11,0	780	-4.4	0.9	1.2 ± 1.2	1.3 ± 1.2
11,1	2144	-3.4	0.2	1.3 ± 1.3	1.3 ± 1.4
11,2	1008	-5.2	0.4	1.4 ± 1.4	1.4 ± 1.5
11,3	974	-4.1	0.9	1.1 ± 1.4	1.3 ± 1.4
11,4	420	-5.7	0.5	1.3 ± 1.5	1.2 ± 1.3
11,5	1782	-4.3	0.7	1.1 ± 1.2	1.5 ± 1.5
10,0	1176	-2.4	0.1	1.2 ± 1.1	1.1 ± 1.2
10,1	1026	-4.2	0.6	1.6 ± 1.6	1.3 ± 1.2
10,3	758	-5.6	0.4	1.2 ± 1.3	1.4 ± 1.5
10,4	466	-3.4	1.2	1.2 ± 1.2	1.3 ± 1.4
10,6	768	-4.0	0.3	1.1 ± 1.2	1.6 ± 1.6
10,4*	604	-4.0	0.6	1.3 ± 1.2	1.3 ± 1.4

^{a}All the rectification ratios are in the positive bias. For comparison purposes, the values of rectification ratios for n-alkanethiols of analogous length are given. ^{b}Numbering derived from Table 1 and Scheme 1. $^c r = J(+0.5$ V$)/J(-0.5$ V$)$.
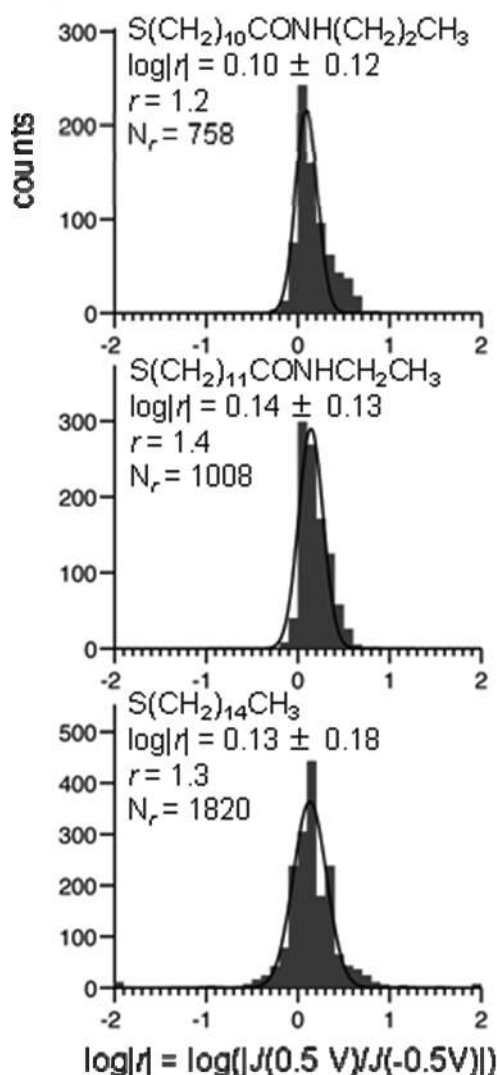
Figure 4. Histograms of $\log|+r|$, where $r = J(0.5\,V)/J(-0.5\,V)$, for compounds with amides at near the terminal group closer to the top electrode and for *n*-alkanethiols. All compounds have 15 non-H atoms in the molecular backbone (excluding sulfur). The first two histograms illustrate the effect of having an amide, and/or shifting the amide by a single carbon, while the bottom histogram is from an *n*-alkanethiol of similar length (same barrier width) for reference.

a difference in work function of the electrodes (E_f Ag = −4.5 eV, EGaIn ≈ −4.3 eV). There is, thus, no evidence that the value or r is different for *n*-alkanethiolates junctions and for compounds where a −CH$_2$CH$_2$− has been replaced with a −CONH− moiety.

The Widths of Histograms for the Measurement of Rectification, *r*, Are Narrower Than Those for Histograms for the Measurements of Current Density, *J*. A comparison of width of histograms of current density, J, to those of the rectification ratio, r, demonstrate again[23] that the former had much larger distributions than the latter. Figure 5 shows examples, and histograms, for three types of molecules; two amides and an alkanethiol. The difference in the width of the distributions in the histograms of J and r reflects, we presume, the fact that the measurements of rectification ratios are self-referencing,[22] i.e. current density on reverse bias is compared to current density in the *same* junction at forward

bias. The junction at one bias thus acts as a reference for the same junction at the opposite bias.

■ CONCLUSIONS

Homologous SAMs Having −CH$_2$CH$_2$−, −CONH−, and −NHCO− Groups Support Statistically Indistinguishable Tunneling Currents. The primary objective of this work was to compare isostructural compounds (**1**, **2**, **3**) with one another, and with *n*-alkanethiolates of the same length, in junctions of the structure Ag^{TS}-SAM//Ga$_2$O$_3$/EGaIn. This work benefits from a comparison with another series of amides of structure **4**; these compounds differ in the position of the amide group, which is closer to the silver electrode in **4** than in **1**−**3**.[56] We draw three conclusions. (i) The amide-based compounds are easier to synthesize than those with an all-carbon backbone, and allow easy synthetic access to a wide range of compounds with which to test hypotheses relating structure to tunneling current. (ii) The presence of the dipole moment embedded in the SAM by the amide has no apparent influence on either the tunneling currents, or, perhaps more significantly for the theory of these systems, on their rectification ratios (r): the values of r for amide-containing and all-hydrocarbon compounds are indistinguishable. (iii) The orbital structure of the −CONH− group is thus, apparently, not sufficiently different from that of a −CH$_2$CH$_2$− group to influence the rate of charge transport by tunneling across these junctions significantly.

The quality of the data we report in this paper is somewhat more broadly distributed than that in previous papers focused on *n*-alkanethiolates, and also on amides of structure **4**.[56] We do not know the reason for this difference yet.

The most important problem in the design of compounds **1**−**3** is the long −(CH$_2$)$_{10-11}$−chain connecting the thiol and the amide group. This length limits the size of the groups, R, that can be placed on the other side of the amide, since for large R groups, values of $J(V)$ become too small to measure reliably with our electrometer. We are thus constrained to use relatively small R groups, where the molecular order of these groups in the SAM is not established, but is almost certainly less than in *n*-alkanethiolates.[51−54,77]

Whatever the reason, the data in Figures 1 and 2 allow us to say that the alkanethiolates and homologous amides are statistically indistinguishable, but do not allow good estimates of values of β for the amides. Making the assumption that values of J_o are similar for amides and for *n*-alkanethioates, however, gives similar values of β ($\beta \approx 1\ n^{-1}$).

Wave Function Engineering. One of the hopes at the beginning of the study of organic tunneling junctions based on SAMs was that variations in the HOMO and LUMO energies of the organic groups—in principle easily achieved through synthesis—would allow the design and generation of tunneling barriers with designed energetic topographies, and the discovery of new types of tunneling behaviors. Variations in the structure of the functional groups included in the SAMs that include common groups (e.g., simple aromatics, amides, saturated hydrocarbons) seem to have little effect on rates of tunneling.[56] The theory of tunneling through junctions containing SAMs is not sufficiently developed at present to give any guidance to these studies, and it is not clear whether this low sensitivity is expected or not. It does, however, empirically constrain the range of organic groups that seem worthwhile to study, when looking for interesting influences on tunneling currents to those that have much larger changes in orbital energies than simple organic functional groups. The
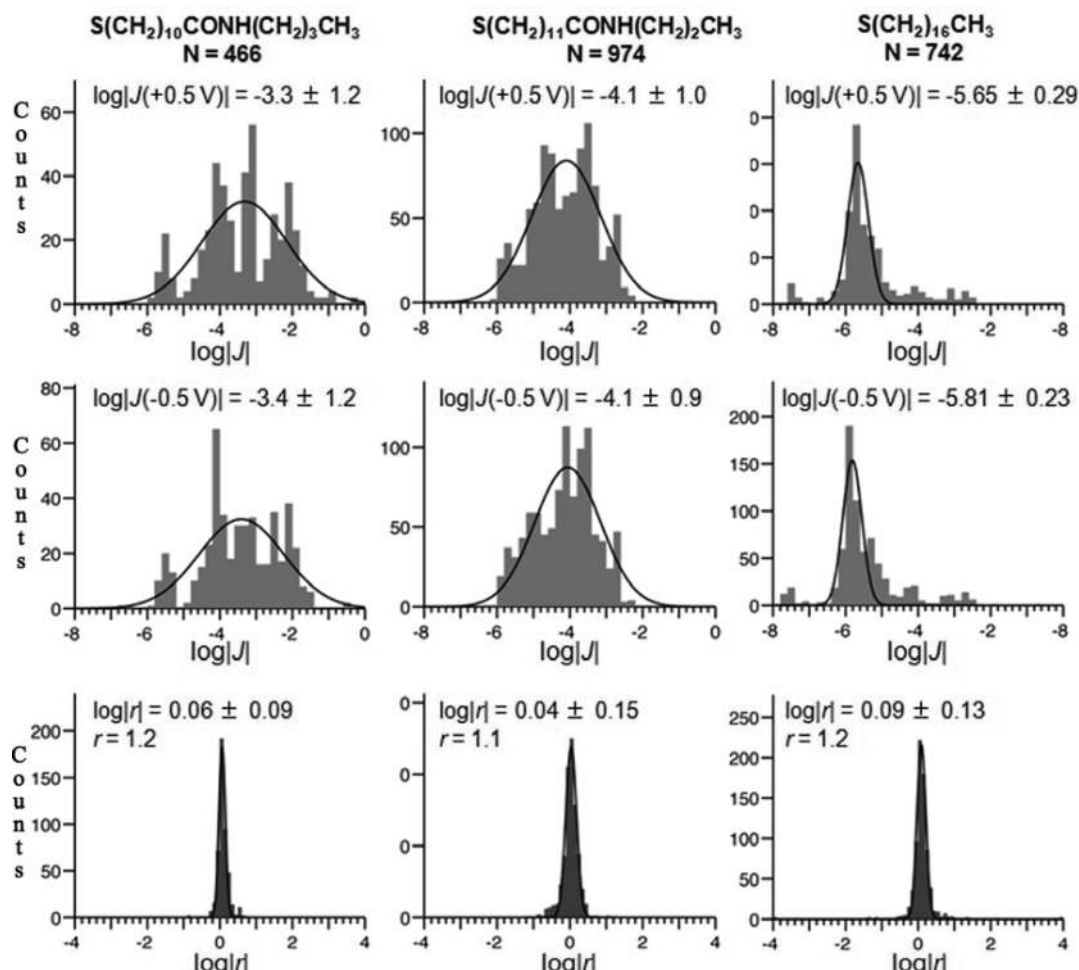
Figure 5. Histograms of log |J| at opposite biases, +0.5 V (top row) and −0.5 V (middle row), above those of log |r| (bottom row), where r = J(+0.5 V)/J(−0.5 V), for two compounds with internal amides along the molecular backbone and an *n*-alkanethiol. The first two rows of histograms illustrate the effect of reversing the applied bias on the distribution of the histograms. The bottom row of histograms gives the histogram of rectification ratios for the three molecules. Comparison down each column illustrates the difference between the width of distributions for current density at opposite applied biases and the rectification ratios.

large rectification observed with terminal ferrocene groups may point toward a useful direction.[22]

Rectification. The largest values of r so far reproducibly observed have been with ferrocene (Fc). The most plausible mechanism underlying these values is based on a difference in mechanism of charge transport at opposite bias in these systems (from pure tunneling to a combination of hopping and tunneling).[21,22] Other mechanisms[22,99,100,102−105] are, of course, in principle possible, and the observation of one mechanism for Fc does not preclude different mechanisms for other compounds. Again, however, the comparison of values of rectification for the range of compounds now available constrains the possible mechanisms. We do not see rectification on embedding the amide dipole near the end of the SAM (away from the silver electrode). Thus, simply embedding even a large dipole in the SAM does not necessarily give large values of rectification (the possible small values that seem consistently to be observed—values of r ≈ 1.2 that are arguably almost indistinguishable from r = 1.0—are probably due to features of the junctions other than the SAM and its orbitals).

In the examination of compounds 1−4, as with other compounds, the values of the standard deviation for rectification are much less than for values of current density.

Thus, whatever causes the dispersion in J(V) largely disappears when the same junction is used for measurements at positive and negative bias. Rectification thus appears to be less sensitive to the details of the structure of the junction than measurements of J(V).

The interplay of the R//Ga$_2$O$_3$ interface and the structure, order, and heterogeneity of the SAM remains unclear. On the one hand, the observation of the odd/even effect in *n*-alkanethiolates, and also—apparently—in the amides **1**, suggest an important role for the interface. On the other, the absence of a large effect on substitution of a nonpolar methyl or *n*-alkyl group by a more polar primary amide [**11,0**] argues against a very sensitive influence of interface on current density. This anomaly requires further experimental work for resolution.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details (materials and methods) and sample ^{1}H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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