Table I. Longitudinal and Transverse Cross-Relaxation Rates for $^{Pro}C_\delta H_2$ and $^{Phe}NH-^{Leu}C_\alpha H$ Protons in Gramicidin S in Me_2SO-d_6

proton pair	temp, °C	$\sigma_\parallel$, s^{-1}	σ_{RF}, s^{-1}	$\sigma_\perp$, s^{-1} [b]	τ_c, ns	$f_\parallel/\sigma_\parallel$, 10^{-9} s^2 [c]	$r_\parallel$, Å [d]	$f_\perp/\sigma_\perp$, 10^{-9} s^2 [e]	$r_\perp$, Å [f]
$C_\delta H \rightarrow C_\delta H'$ [a]	20	−1.8	4.0	4.4	1.9	0.96	1.9	0.98	1.9
	30	−1.3	3.4	3.6	1.5	0.98	2.0	0.98	1.9
	40	−0.79	2.8	3.0	1.2	1.0	2.0	0.97	2.0
	60	−0.27	2.0	2.1	0.77	1.0	2.0	1.1	2.0
$^{Phe}NH \rightarrow {}^{Leu}C_\alpha H$ [a]	20	−0.75	1.6	1.9	1.8	2.1	2.2	2.1	2.2
	30	−0.40	1.4	1.6	1.1	1.7	2.1	1.8	2.1
	40	−0.20	1.0	1.2	0.8	1.9	2.2	1.9	2.2
	60	~0	0.9	1.0	0.6			1.9	2.2

[a] Offsets from rf carrier: $^{Pro}C_\delta H$, −357 Hz; $^{Pro}C_\delta H'$, −662 Hz; ^{Phe}NH, 1302 Hz; $^{Leu}C_\alpha H$, −50 Hz; γB_{SL} = 2174 Hz. [b] From eq 3. [c] $f_\parallel = (6/(1 + 4\omega_0^2\tau_c^2) - 1)\tau_c$. [d] From eq 2. [e] $f_\perp = (3/(1 + \omega_0^2\tau_c^2) + 2)\tau_c$. [f] From eq 1.

To test this we measured $\sigma_\parallel$ and $\sigma_\parallel$ as a function of temperature for different pairs of protons in the cyclic decapeptide Gramicinin S in Me_2SO-d_6. The experiments were done at 300 MHz by using one-dimensional difference techniques. To determine $\sigma_\parallel$, a weak 180° pulse (20 ms) from the decoupler was used to selectively invert one of the proton lines in the spectrum. Following a delay 10–100 ms for cross-relaxation, a strong nonselective 90° pulse was applied and the FID was collected. On alternate scans, the frequency of the decoupler pulse was offset by ~50 Hz and the FID was subtracted from memory. Fourier tranformation of the difference FID yielded a spectra containing only the inverted line and "cross-peaks" from cross-relaxation. For σ_{RF}, the pulse sequence was modified by replacing the delay and 90° pulse with a 90° pulse followed immediately by a spin-locking pulse (γB_{SL} = 2100 Hz) shifted in phase by 90° and applied for times ranging from 10 to 100 ms.[6] The cross-relaxation rates were taken as the initial slope of the ratio of the "cross-peak" to inverted peak intensities vs. the delay or the spin-locking time.[7] The transverse cross-relaxation rate $\sigma_\perp$ was calculated by using eq 3 and the observed values of $\sigma_\parallel$ and σ_{RF}.

Cross-relaxation rates for the geminal pair of proline C_δ protons and for the phenylalanine NH-leucine $C_\alpha H$ pair are listed in Table I, together with the correlation times and internuclear distances derived from these rates. In view of the fact that no a priori assumptions were made about distances or correlation times, these results are quite acceptable. The PheNH–Leu$C_\alpha H$ distance is in excellent agreement with that predicted by minimum-energy calculations and molecular models.[8] Even the apparent lengthening of the distance between the C_δ geminal protons by 0.2 Å is consistent with what is known about the internal dynamics of proline-ring deformations. According to the "model free" approach,[9] internal molecular motion occurring at rates much faster than the overall rotational tumbling of the molecule leads to a diminution of $\sigma_\parallel$ and σ_{RF} by a factor, $\mathcal{S}^2$. Consequently, $r_{app}^{-6} = \mathcal{S}^2 r_{true}^{-6}$. Assuming r_{true} = 1.8 Å, we calculate a value for $\mathcal{S}$ of 0.6. This agrees well with the value of 0.57 calculated by using parameters of London[10] for proline ring dynamics and ^{13}C relaxation.

Our results also show that the correlation times for cross-relaxation of the $NHC_\alpha H$ pair are approximately 0.7 times shorter than those for the C_δ geminal pair. Such differences could arise if there are internal modes with correlation times comparable to the rotational correlation time or if the rotational motion is anisotropic and the internuclear vectors have significantly different orientations with respect to the axis of the diffusion tensor.

We also note that if one calculates $r_{NHC_\alpha H}$ using the accepted separation of the C_δ protons for calibration, one finds r = 2.1 ± 0.1 Å. Although this procedure is clearly invalid for gramicidin S, it yields a perfectly acceptable result owing to a fortuitous cancellation of two erroneous asssumptions.

Recently, Mirau and Bovey[11] described a method for determining τ_c on the basis of the ratio of the nonselective and selective spin–lattice relaxation rates, and it is applicable over the same range of τ_c as ours (i.e., for molecules of MW = 1–3 kdaltons). It differs in that one must assume that spin–lattice relaxation is purely dipolar in origin; an assumption that may not be generally valid. Nonetheless, both methods provide useful access to internuclear distances which are unencumbered by a priori assumptions.

Acknowledgment. We have benefited from helpful comments by A. Bax and V. Sklenar.

---

(6) Offsets and rf field strength were choosen to minimize homonuclear Hartmann–Hahn (HOHAHA) transfer; see: Davis, D. G.; Bax, A. *J. Am. Chem. Soc.* **1985**, *107*, 2820–2821.

(7) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546–4554.

(8) Dygert, M.; Go, N.; Scheraga, H. A. *Macromolecules* **1975**, *8*, 750–761.

(9) Lipari, G.; Szabo, A. *J. Am. Chem. Soc.* **1982**, *104*, 4546–4559.

(10) London, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 2678–2685.

(11) Mirau, P. A.; Bovey, F. A. *J. Am. Chem. Soc.* **1986**, *108*, 5130–5134.

Coordination Chemistry of Semiconductor Photoelectrodes: Reactions of Etched n-GaAs with Co(III) Complexes

Ian L. Abrahams, Bruce J. Tufts, and Nathan S. Lewis*

Department of Chemistry, Stanford University
Stanford, California 94305

Received December 11, 1986

We report studies of the reactivity of n-GaAs surfaces with transition-metal complexes. Generally, adsorption of metal ions at semiconductor junctions has been observed to increase carrier trapping rates.[1] A notable exception is the improved performance of n-GaAs interfaces after exposure to acidic aqueous solutions of Ru(III) ions and other metal cations,[2] but little information is available regarding the chemistry of these surface treatments. Except for systems in which metal ions act as precursors for the deposition of metals or metal alloys,[3] no information is available regarding the oxidation state or chemical environment of chemisorbed transition-metal complexes on semiconductor electrodes. Possible but undocumented mechanisms of metal ion attachment to the semiconductor surface include electrostatic binding, ligand substitution processes, and redox reactions. To explore the various

---

* Author to whom correspondence should be addressed.

(1) (a) Many, A.; Goldstein, Y.; Grover, N. B. *Semiconductor Surfaces*, North Holland: Amsterdam, 1965. (b) Frankl, D. R. *J. Electrochem. Soc.* **1962**, *109*, 238. (c) Boddy, P.; Brattain, W. H. *J. Electrochem. Soc.* **1962**, *109*, 812.

(2) (a) Parkinson, B. A.; Heller, A.; Miller, B. *J. Electrochem. Soc.* **1979**, *126*, 954; *Appl. Phys. Lett.* **1978**, *33*, 521. (b) Heller, A. *ACS Symp. Ser.* **1981**, *No. 146*, 57. (c) Frese, K. W., Jr.; Madou, M. J.; Morrison, S. R. *J. Electrochem. Soc.* **1981**, *128*, 1939. (d) Ludwig, M.; Heymann, G.; Janietz, P. *J. Vac. Sci. Technol.* **1986**, *B4*, 485. (e) Allongue, P.; Cachet, H. *J. Electrochem. Soc.* **1984**, *131*, 2861.

(3) (a) Fan, F.-R.; Hope, G.; Bard, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 220. (b) Howe, A. T. *J. Chem. Soc., Chem. Commun.* **1983**, 1407. (c) Bruce, J. A.; Murahashi, T.; Wrighton, M. S. *J. Phys. Chem.* **1982**, *86*, 1552. (d) Aharon-Shalom, E.; Heller, A. *J. Electrochem. Soc.* **1982**, *129*, 2865. (e) Kautek, W.; Gobrecht, J.; Gerischer, H. *Ber. Bunsenges. Phys. Chem.* **1980**, *84*, 1034.

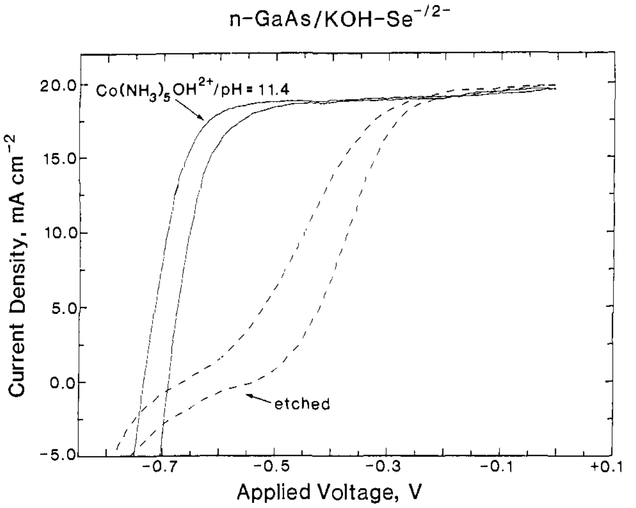


Figure 1. Current–voltage properties (50 mV/s) of (100) n-GaAs electrodes in 1.0 M KOH–1.0 M K_2Se–0.01 M K_2Se_2. The light intensity (ELH-type W–halogen irradiation) was adjusted to yield photocurrent densities of 20.0 mA/cm^2. The electrodes were etched in 4:1:1 $H_2SO_4/H_2O_2/H_2O$ for 10 s and rinsed with H_2O before use: (---) etched surface; (—) etched surface which was then immersed in a 0.010 M solution of $[Co(NH_3)_5(H_2O)]Br_3$ at pH 11.4 for 60 s, rinsed with H_2O, and dried under N_2 before evaluation in the KOH–Se$^{-/2-}$ cell. The *I–V* properties were stable (±5%) for passage of over 2000 C/cm^2 of charge through the interface under operation at the maximum power point.

possible modes of reaction, we have investigated the chemistry of n-GaAs surfaces in contact with aqueous solutions of Co(III) complexes.

Exposure of (100)-oriented n-GaAs to an aqueous solution of $Co(NH_3)_5(H_2O)^{3+}$ (0.010 M) in base (pH 11.4) yields dramatic, persistent improvements in the I–V characteristics of the n-GaAs/KOH–Se$^{-/2-}$ junction (Figure 1). Extremely similar *I–V* behavior is obtained from 0.010 M solutions (pH ≥10) of $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5N_3^{2+}$. In the pH range studied (0< pH <12), all of these Co(III) complexes are inert to substitution on the timescale of minutes.[4] We thus rule out ligand substitution processes on the Co(III) complex as the mode of metal ion attachment in this system.

Two alternative possibilities of adsorption are electrostatic binding of cations and redox reactions to produce a more labile oxidation state than Co(III).[5] Previous success with various metal cations[2a] suggests that electrostatic binding might be an important feature of the metal ion adsorption on GaAs surfaces. We observe that none of the substitution-inert Co(III) complexes yield improvements in *I–V* behavior when the solution has a pH <4, indicating that electrostatic binding of cations is not an effective adsorption mechanism for etched (100) n-GaAs in acidic media. Consistently, XPS spectra[6] of n-GaAs surfaces exposed to pH <4 Co(III) solutions exhibited no detectable Co signal. After exposure of (100) n-GaAs single crystals to Co(III) solutions in neutral or basic media, XPS analysis of the n-GaAs displayed peaks at binding energies of 782.0 and 798.3 eV, with satellites at 787.6 and 803.9 eV. This spectrum clearly indicates an oxidation state of Co(II) for the adsorbed metal ion.[7] Consistent with the expected labilization of Co(II), we observed no XPS signals (above base line N) from N atoms of any remaining NH_3 ligands, nor did we observe Cl or Br signals when the initial Co(III) complex was $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_5Br]Br_2$, or $[Co(NH_3)_5N_3]Br_2$. We note that the XPS spectrum of $Co(OH)_2$ also exhibits peaks at 782 and 798 eV,[7c] suggesting that the GaAs-bound Co(II) is in a very similar ligand environment to that of the octahedral Co(II) in $Co(OH)_2$. Consistently, treatment of n-GaAs photoanodes with aqueous basic Co(II) also yields improved *I–V* properties. Furthermore, Co(II) has been shown to be an effective electrocatalyst for In_2O_3, CoS,[8] and p-GaAs electrodes in KOH–S$^{-/2-}$ and KOH–Se$^{-/2-}$ solutions.

Further evidence supporting the redox process has been obtained by investigating the reactions of GaAs powder. We have observed quantitative reduction to the M(II) oxidation state of $Ru(bpy)_3^{3+}$ ($E°' = +1.02$ V vs. SCE), $Co(bpy)_3^{3+}$ ($E°' = +0.10$ V), and $Ru(NH_3)_5(py)^{3+}$ ($E°' = +0.06$ V) for 0< pH <11; however, no reduction of *N,N'*-dibenzyl-4,4'-bipyridinium ($E°' = -0.60$ V) was observed in this pH range. These observations are consistent with the calculated redox potential for the reaction $GaAs + 2H_2O \rightarrow Ga^{3+} + HAsO_2 + 3H^+ + 6e^-$ ($E°' = -0.23$ V at pH 0)[9] and also indicate that the GaAs possesses sufficient reducing power to produce Co(II) from our Co(III) complexes ($E°'$(irrev) ~ −0.18 V).[10] Further chemical support for this notion is the observation that exposure of GaAs powder to a pH >8 solution of $Co(NH_3)_6^{3+}$ led to depletion of the Co(III) complex from the solution, and subsequent treatment of the GaAs powder with SCN^- produced a quantitative recovery of the reacted Co(III) as the $Co^{II}(SCN)_4^{2-}$ species.[11] Use of the substitution-inert $Co(bpy)_3^{2+}$ cation at pH <11 yielded no detectable chemisorption of Co onto either GaAs powders or n-GaAs photoanodes, indicating that electrostatic binding alone is not an effective mechanism for Co chemisorption or for improvement of the n-GaAs *I–V* properties.

For $Co(NH_3)_6^{3+}$-exposed, matte-textured[2a] n-GaAs surfaces (MOCVD grown, $L_p > 5$ μm; $N_D = 2 \times 10^{17}$ cm^{-3}) under 88 mW/cm^2 of ELH-type tungsten halogen illumination,[12] we have observed short-circuit photocurrent densities of 23 mA/cm^2, open-circuit voltages of 730–740 mV, fill factors of 0.60–0.70, and efficiencies of 12.5 ± 1%. These efficiencies represent relative improvements of 1.15–1.20 over the efficiency for n-GaAs/Ru^{3+} surfaces under identical photocurrent densities.[2,12]

This work indicates that the coordination chemistry of semiconductor interfaces can elucidate the chemical nature of metal ion binding. These studies are particularly relevant to the metal ion induced changes in surface recombination velocity at n-GaAs/air interfaces.[13] We emphasize that although the Co ion may initially be bound in a particular oxidation state and environment, subsequent chemical changes upon exposure to KOH–Se^{2-} will preclude general correlations between decreases in surface recombination rates at GaAs/air interfaces and improvements in *I–V* behavior in KOH–Se^{2-} solutions.[14] Efforts are under way to elucidate the nature of this interaction, as well as to determine

---

[4] Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1967.

[5] (a) Farley, K. J.; Dzombak, D. A.; Morel, F. M. M. *J. Colloid Interface Sci.* **1985**, *106*, 226. (b) Perona, M. J.; Leckie, J. O. *J. Colloid Interface Sci.* **1985**, *1*, 64. (c) White, A. F.; Yee, A. *Geochim. Cosmoch. Acta* **1985**, *49*, 1263.

[6] Spectra were obtained on a VG ESCALAB II with Al Kα irradiation referenced relative to a Ag foil (Ag 3d doublet at 368.20 and 374.20 eV). The instrumental resolution is 1.0 eV.

[7] (a) Frost, D. C.; McDowell, C. A.; Woolsey, I. S. *Mol. Phys.* **1974**, *27*, 1473; *Chem. Phys. Lett.* **1972**, *17*, 320. (b) Haraguchi, H.; Fujiwara, K.; Fuwa, K. *Chem. Lett.* **1975**, *1975*, 409. (c) Chuang, T. J.; Brundle, C. R.; Wandelt, K. *Thin Solid Films* **1978**, *53*, 19.

[8] (a) Abrahams, I. L.; Casagrande, L. G.; Rosenblum, M. D.; Rosenbluth, M. L.; Santangelo, P. S.; Tufts, B. J.; Lewis, N. S. *Nouv. J. Chim.*, in press. (b) Hodes, G.; Manassen, J.; Cahen, D. *J. Electrochem. Soc.* **1980**, *127*, 544.

[9] (a) Memming, R. *J. Electrochem. Soc.* **1978**, *125*, 117. (b) Thurmond, C. D.; Schwartz, G. P.; Kammlott, G. W.; Schwartz, B. *J. Electrochem. Soc.* **1980**, *127*, 1366. (c) Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solution*; Pergamon: New York, 1966.

[10] Bartelt, H.; Landazury, S. *J. Electroanal. Chem.* **1969**, *22*, 105.

[11] Upor, E.; Mohai, M.; Novak, G. *Comprehensive Analytical Chemistry*; Elsevier: Amsterdam, 1985, Vol. 20, p 184.

[12] The ELH bulb has been shown to be an accurate solar simulator for n-GaAs/KOH-Se$^{-/2-}$ cells: Gronet, C. M.; Lewis, N. S. *J. Phys. Chem.* **1984**, *88*, 1310.

[13] (a) Nelson, R. J.; Williams, J. S.; Leamy, H. J.; Miller, B.; Parkinson, B. A.; Heller, A. *Appl. Phys. Lett.* **1980**, *36*, 76. (b) Heller, A. *Acc. Chem. Res.* **1981**, *14*, 154. (c) No change in surface recombination velocity (>10^5 cm/s; steady-state luminescence measurement) was observed in this work for Co-treated n-GaAs surfaces, in contrast to the Ru-induced improvements observed in ref 13a.

[14] XPS spectra show pronounced changes in the Co 2p region upon exposure of $Co(NH_3)_6^{3+}$-treated n-GaAs to KOH-Se$^{-/2-}$ solutions and displayed peaks at binding energies of 778.8 and 793.3 eV (and no satellite structure), clearly indicating chemical reactions of the bound Co complex with the KOH-Se^{2-} electrolyte: Abrahams, I. L.; Tufts, B. J.; Lewis, N. S., manuscript in preparation.

the equilibrium constants and kinetics for metal ion binding to GaAs.

Acknowledgment. We acknowledge support from the National Science Foundation, CHE-12692, for this work. N.S.L. acknowledges support under the Presidential Young Investigator program (CHE-8352151) with matching funds from Monsanto, Exxon, Mobil, Sohio, and IBM. N.S.L. also acknowledges support as a Dreyfus Teacher-Scholar and an Alfred P. Sloan Foundation Fellow. We thank R. Dominguez and C. M. Gronet for assistance with some of the experiments in this study and Dr. C. R. Lewis of Varian Associates, Palo Alto, CA, for a generous supply of GaAs.

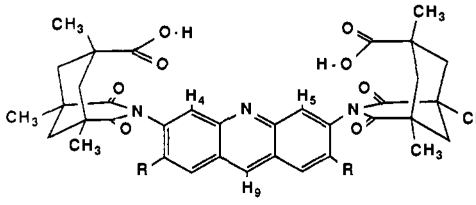
Molecular Recognition: Size and Shape Specificity in the Binding of Dicarboxylic Acids

J. Rebek, Jr.,* D. Nemeth, P. Ballester, and F.-T. Lin

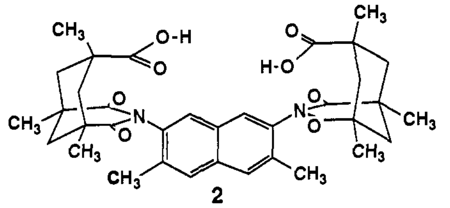
Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Received August 4, 1986
Revised Manuscript Received March 23, 1987

We recently introduced[1] the model receptors **1** and **2** and gave evidence of their unique binding capacities.[2] In these structures two carboxyl groups converge on a molecular cleft in a manner similar to the convergence of the carboxyl functions in enzymes such as lysozyme[3] and the aspartic proteinases.[4] This feature accounts for the unusual acid dissociation constants of the diacids[5] and is the crucial element in their ability to recognize smaller molecules of complementary size, shape, and functionality.[6] The aromatic spacer groups in **1** and **2** prevent the formation of intramolecular hydrogen bonds between the opposing carboxyl groups, yet these functions are ideally positioned for intermolecular hydrogen bonding; here we report how these receptors interact with carboxylic acids.



1a R = H
1b R = CH_3



2

A solution of **1b** in $CDCl_3$ (10^{-3} M) dissolves solid oxalic acid (pK_{a1} = 1.2[8]), a substance otherwise quite insoluble in this medium, and ^{13}C NMR[7] established a 1:1 stoichiometry for the complex.

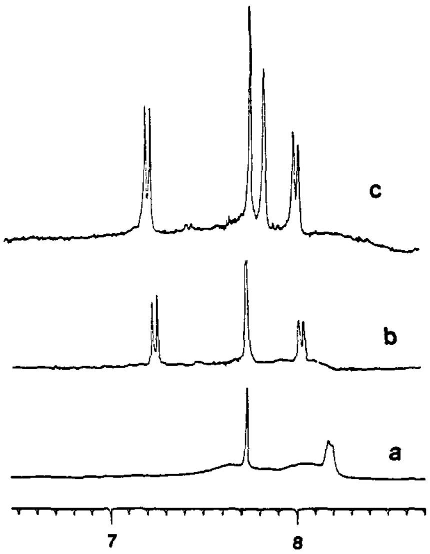


Figure 1. (a) Ambient temperature (297 K) 300-MHz ^{1}H NMR spectrum of **3** broadened by rotation; (b) spectrum after the addition of 2 equiv of glutaric acid at 297 K; (c) as in (b) but at 210 K.

Similar behavior was observed by proton NMR for malonic acid (pK_{a1} = 2.9), its C-substituted derivatives, and maleic (pK_{a1} = 1.8) or phthalic acids (pK_{a1} = 2.9). Fumaric (pK_{a1} = 3.0), succinic (pK_{a1} = 4.2), or glutaric (pK_{a1} = 4.3) acids were unaffected under these conditions. At first glance, these results appear to establish the pK_a of **1**·H$^+$ as ≤ 3, since only the stronger acids are complexed. The downfield shift of H_9 (8.7 → 9.2 ppm) seen in the presence of the stronger acids is in accord with partial protonation of the acridine nitrogen; stronger acids such as picric or *p*-toluenesulfonic also cause this proton to shift (9.4 ppm).

Protonation may be a necessary element in the recognition of acids by **1b** but this receptor has more to offer than mere basicity. Specifically, the picrate of **1b** also dissolves oxalic or malonic acid in $CDCl_3$, and this process results in the release of free picric acid (pK_a 0.4). In other experiments the complex of **1b** with malonic acid was treated with excess picric acid in $CDCl_3$. Only after 6 equiv of the stronger acid were added did the weaker malonic acid begin to separate from solution. These experiments establish that **1**·H$^+$ provides some special stabilization to the conjugate bases of oxalic and malonic acids. That is, these dicarboxylic acids appear stronger than picric acid when **1** is present.

What is the nature of this special stabilization? Two lines of evidence bear on this issue. First, compounds[9] **1a** and **3** provide some dynamic evidence. In these, rotations about the C_{aryl}–N_{imide} bonds are facile at room temperature and result in broadened ^{1}H NMR spectra. Figure 1a shows the ambient temperature spectrum of **3**; simple salts of **1a** such as the picrate show similar line broadening. At low temperature, complex spectra are observed for **1a** (or its picrate) and for **3** (with or without HOAC) since interconversions between the three possible conformations become slow. However, in the presence of dicarboxylic acids of appropriate size and shape the spectra are sharpened and are no longer temperature dependent.

Figure 1b shows the room temperature spectrum of **3** in contact with glutaric acid and Figure 1c shows the same system at 210 K. Similar behavior is seen in the spectra of **1a** in the presence of 1 equiv of oxalic or malonic acids.[10] Binding to diacids of appropriate size, shape, and pK_a restricts **1a** or **3** to the conformations featuring convergent carboxyls as shown in **4**. Only these

---

(1) Rebek, J., Jr.; Marshall, L.; Wolak, R.; Parris, K.; Killoran, M.; Askew, B.; Nemeth, D.; Islam, N. *J. Am. Chem. Soc.* **1985**, *107*, 7476-7481.

(2) Rebek, J., Jr.; Askew, B.; Islam, N.; Killoran, M.; Nemeth, D.; Wolak, R. *J. Am. Chem. Soc.* **1985**, *107*, 6736-6738.

(3) Blake, C. C. F.; Koenig, D. F.; Mair, G. A.; North, A. C. T.; Phillips, D. C.; Sarma, V. C. *Nature (London)* **1985**, *206*, 757.

(4) Pearl, L.; Blundell, T. *FEBS Lett.* **1984**, *174*, 96-101.

(5) Rebek, J., Jr.; Duff, R. J.; Gordon, W. E.; Parris, K. *J. Am. Chem. Soc.* **1986**, *108*, 6068-6069.

(6) Rebek, J., Jr.; Askew, B.; Nemeth, D.; Parris, K. *J. Am. Chem. Soc.* **1987**, *109*, 2432-2434.

(7) The ^{13}C oxalate resonance appears at 161.5 ppm in the complex (Me_2SO–$CDCl_3$ at 77.09 ppm) where free oxalic acid appears at 159.5 ppm in the same medium.

(8) Acid dissociation constants are from: Bonhomme, G.; Juillard, J. *J. Chim. Phys.* **1974**, *71*, 1097-1100. *CRC Handbook of Chemistry and Physics*, 60th ed.; CRC Press: Boca Raton, FL, 1979.

(9) Rebek, J., Jr.; Nemeth, D. *J. Am. Chem. Soc.* **1985**, *107*, 6738.

(10) For **1a**–oxalate in $CDCl_3$ signals were at 7.35, d; 8.15, d; 8.6, s; and 9.3 ppm, s, and for **1a**–malonate at 7.35, d; 8.1, d; 8.45, s; and 9.3 ppm, s.

0002-7863/87/1509-3474$01.50/0 © 1987 American Chemical Society