$$\lim_{n \to \infty} \langle r^2 \rangle_0 / nl^2 = \infty \text{ and } \lim_{n \to \infty} \langle \mu^2 \rangle n / m^2 = 0$$

An increase in temperature increases the *gauche* population about bonds such as $i - 1$, i, and $i + 2$ in Figure 1, but either leaves unchanged or decreases the *gauche* population about bonds such as $i + 1$ and $i + 3$. The former effect predominates, giving rise to a negative temperature coefficient of $\langle r^2 \rangle_0$, which is increased in magnitude by the concomitant increase in population of compact $g^{\pm}g^{\mp}$ states about some bond pairs in the chain. The molecular basis for the increase in $\langle \mu^2 \rangle$ with temperature is more difficult to visualize, but the primary effect is the increase in the number of *gauche* states about bonds such as $i - 1$, i, and $i + 2$ as the temperature is raised.

According to this general analysis, the form of the poly(tetramethylene oxide) chain of minimum *intra*molecular energy is ($ttg^{\pm}tg^{\pm}$), where the bonds in the repeat unit are designated in the order given in Figure 1. The intramolecular energy difference between this form and the planar zigzag (*ttttt*) conformation is small, however, or possibly zero. The all-*trans* form of the chain would be more efficiently packed into a crystalline lattice than would the ($ttg^{\pm}tg^{\pm}$) form, which apparently represents an unusual helical arrangement having a large number of monomer units per turn of the helix. X-Ray diffraction studies[14] on this polymer show that the chains are in the all-*trans* conformation in the crystalline lattice, thus indicating the *inter*molecular interactions may be of importance when two or more forms of the chain are of low, and approximately equal, intramolecular energies.

Although the theoretical calculations are in good agreement with the dipole moment obtained on poly(tetramethylene oxide) chains in the bulk, amorphous state, considerably more experimental results are required for a thorough evaluation of the model. Of particular importance would be determinations of $\langle r^2 \rangle_0 / nl^2$ and $\langle \mu^2 \rangle / nm^2$ for the chain in dilute solution; the temperature coefficient of both of these quantities and the dependence of $\langle \mu^2 \rangle / nm^2$ on chain length are also of obvious interest.

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An Electron Spin Resonance Study of the Reduction of Polynitromesitylenes and -durenes[1,2]

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Abstract: Bernal and Fraenkel have reported a series of unidentified free radicals obtained by electrolytic reduction of trinitromesitylene, dinitromesitylene, and dinitrodurene. These radicals are shown to be nitroamine anions corresponding to the reduction of one nitro group. Complete analysis of the proton hyperfine structure observed in the esr spectra is reported. The reduction reactions of *m*- and *p*-dinitrobenzene and the spectra of the *m*- and *p*-nitroaniline anions are reported for comparison. Unidentified radicals were detected on reduction of trinitro-, aminodinitro-, and dinitromesitylene as well as dinitroisodurene. These radicals are apparently due to side reactions, the nature of which is discussed. A mechanism for the observed reduction of dinitrodurene to the diaminodurene cation is proposed. A correlation of the spin-density distribution in hindered nitrobenzenes with polarographic half-wave potentials is presented.

In recent years, electron spin resonance (esr) has proved to be a useful tool in characterizing the reactions of aromatic radical ions in solution. Numerous examples of substitution, rearrangement, and elimination reactions have been found by this technique.[4] In an investigation of the esr spectra of several polynitro aromatic anions, Bernal and Fraenkel[5] found that by electrolyzing solutions at potentials more negative than those used to produce the monoanions, new paramagnetic species were formed which had fewer equivalent nitro groups than the starting material. These radicals were apparently not simple elimination or rearrangement products, since, for example, the second radical obtained from reduction of dinitrodurene is not the nitrodurene anion,[5] nor, as we shall show, is it the nitroisodurene or pentamethylnitrobenzene anion.

Qualitatively, these results are similar to those of Ward[6] who prepared polynitromesitylene radicals by chemical reduction in dimethoxyethane solution and observed a hyperfine splitting from a single nitrogen nucleus. Ward suggested that his results indicated a tight ion pair such that an alkali metal ion traps the spin density on a single nitro group. This interpreta-

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(3) Du Pont Teaching Fellow, 1964–1965.

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(5) I. Bernal and G. K. Fraenkel, *J. Am. Chem. Soc.*, **86**, 1671 (1964).

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tion now seems well established on the basis of recent work by Symons.[7]

We shall show that electrolytic reduction of polynitromesitylenes and -durenes leads to the nitroamine corresponding to reduction of one nitro group to an amino group rather than to the elimination and substitution reactions found with the simpler nitrobenzenes.[8]

Experimental Section

Chemicals. Nitromesitylene, dinitromesitylene, dinitrodurene, and diaminodurene were obtained from commercial sources and recrystallized before use. Trinitromesitylene was prepared by nitration of dinitromesitylene, mp 238–238.5° (lit.[9] 235°). Dinitroisodurene was prepared by nitration of isodurene, mp 183–184° (lit.[10] 183°). Pentamethylnitrobenzene was prepared by nitration of the acetoxymercury derivative of pentamethylbenzene,[11] mp 151–153° (lit.[12] 154°). Aminodinitromesitylene, mp 190–191° (lit.[13] 193°), diaminonitromesitylene mp 184–185° (lit.[13] 184°), aminonitromesitylene, mp 72–73° (lit.[14] 74°), aminonitrodurene, mp 162–163° (lit.[15] 162°), and aminonitroisodurene, mp 137–138° (lit.[10] 140°), were prepared by reduction of the appropriate polynitro compound with sodium polysulfide following the procedure of Birtles and Hampson.[15,16]

The preparation of the solvent, N,N-dimethylformamide (DMF), and the supporting electrolyte, tetra-*n*-propylammonium perchlorate, have been described previously.[17] The purity of the DMF was checked polarographically and by measuring its conductance. Polarographically the DMF and the supporting electrolyte were found to be less than 10^{-4} *M* in reducible impurities. The equivalent conductance of a routinely prepared batch of DMF was 3 × 10^{-8} ohm^{-1} cm^{-1} at 25°. Thomas and Rochow[18] have estimated that a conductance of 10^{-7} ohm^{-1} cm^{-1} corresponds to 10^{-3} *M* concentration of "proton releasing impurities."

Apparatus. The polarographic data were obtained with the three-electrode polarograph similar to that described by Kelley, Fisher, and Jones,[19] suitably modified to permit oscillopolarography.[20] The potentials were measured with respect to an aqueous saturated calomel electrode (sce) and are reproducible to ±5 mv.

The esr spectra were obtained with a superheterodyne spectrometer employing 1-kc field modulation similar to that described by Hirshon and Fraenkel.[21] The splitting constants were measured from a field-calibrated strip-chart recording to a precision of ±20 mgauss. Artificial line sharpening was obtained by the field modulation technique of Glarum.[22]

Electrolysis. Radical anions were prepared by controlled potential electrolysis in a cylindrical glass cell with a volume of about 1 cm^3, having a mercury cathode area of about 1 cm^2.[23] The applied potential was measured with respect to a separate mercury pool electrode. This electrode was easily reproducible to ±0.1 v, but its potential with respect to the sce was +0.1 to +0.4 v, depending upon the compound being investigated.

Samples were electrolyzed for periods ranging from 5 to 30 min to obtain optimum signal-to-noise ratio and the narrowest lines, and then forced through a short glass capillary tube into the sample tube in the microwave cavity. The DMF solutions in this work were all 1–2 m*M* in the compound being investigated, 0.1 *M* in tetra-*n*-propylammonium perchlorate, and were deaerated with prepurified nitrogen prior to electrolysis.

Results

The dc polarographic half-wave potentials for all compounds studied are given in Table I. The first reduction potential in every case except dinitrodurene corresponds to a one-electron reduction shown to be reversible by oscillopolarography, and for which $\mathcal{E}_{3/4} - \mathcal{E}_{1/4}$ is approximately 56 mv. The second waves of the *m*-dinitropolymethyl compounds are one-electron reversible reductions at voltage sweep rates greater than 20 v/sec, but correspond to multielectron reductions at slower rates. These waves are enhanced by the addition of water or acid.

Table I. Polarographic Half-Wave Potentials

Compound	$\mathcal{E}_{1/2}$[a]
Nitrobenzene	−1.082
m-Dinitrobenzene	−0.806, −1.245
p-Dinitrobenzene	−0.543, −0.872
m-Nitroaniline	−1.150
p-Nitroaniline	−1.335
Trinitromesitylene	0.928[b]
Dinitromesitylene	−1.153, −1.50
Dinitrodurene	−1.158[c]
Dinitroisodurene	−1.182, −1.50
Aminodinitromesitylene	−1.225, −1.52
Nitromesitylene	−1.380
Pentamethylnitrobenzene	−1.428
Aminonitromesitylene	−1.458
Aminonitroisodurene	−1.472
Diaminonitromesitylene	−1.487
Aminonitrodurene	−1.531
Diaminodurene	0.099[d]

[a] Half-wave potentials *vs.* sce; estimated precision ±0.05 v. [b] Polarographic maximum at −1.2 v, distorted one-electron waves at −1.4 and −1.7 v. [c] Two-electron wave. [d] Oxidation wave.

The nuclear hyperfine splitting constants of the various anion radicals discussed below are given in Table II.

Trinitromesitylene. Reduction at −1.0 v (*vs.* mercury pool) gave a blue solution which displayed an esr spectrum identical with that reported by Glarum and Marshall.[24] Reduction at −1.1 v gave a brown solution which displayed a weak asymmetric spectrum, apparently due to more than one species. The spectrum consisted of approximately 140 lines extending over 41 gauss, and has not been interpreted. At potentials more negative than −1.4 v, a red solution was obtained which gave a strong esr spectrum identical with that reported by Bernal and Fraenkel[5] and with that of the aminodinitromesitylene anion.

Aminodinitromesitylene. Reduction at −1.3 v gave a purple solution and an esr spectrum exhibiting a very pronounced alternation of line widths;[5,25] the sharpest lines were about 150 mgauss wide.[26] The interpretation of methyl proton hyperfine splittings was unambiguous, but no splittings assignable to the amino group were observed. By analogy to *m*-nitroaniline (*vide*

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[19] M. T. Kelley, D. J. Fisher, and H. C. Jones, *Anal. Chem.*, **31**, 1475 (1959).

[20] D. E. Smith, *ibid.*, **35**, 1811 (1963).

[21] J. M. Hirshon and G. K. Fraenkel, *Rev. Sci. Instr.*, **26**, 34 (1955).

[22] S. H. Glarum, *ibid.*, **36**, 771 (1965).

[23] P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963).

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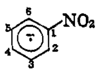
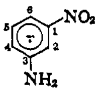
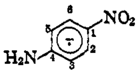
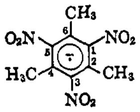
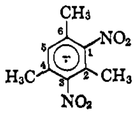
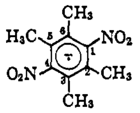
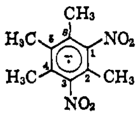
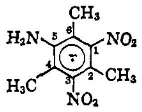
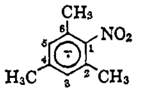
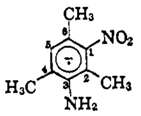
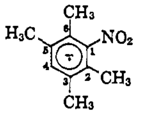
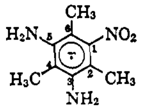
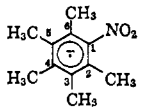
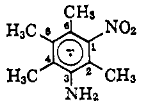
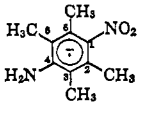
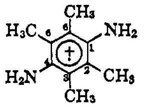
[25] J. H. Freed and G. K. Fraenkel, *ibid.*, **41**, 699 (1964).

[26] Line widths measured between derivative extrema.

Table II. Nuclear Hyperfine Splitting Constants

Starting material	Radical	Ring position					
		1	2	3	4	5	6
Nitrobenzene^a		9.70	3.36	1.07	4.03	1.07	3.36
m-Nitroaniline *m*-Dinitrobenzene		10.13	3.01^c	0.21 (N) 0.31 (H)	3.62^c	0.96^c	3.46^c
p-Nitroaniline		11.49	3.38^c	1.08^c	1.08 (N) 0.89 (H)	1.08^c	3.83^c
Trinitromesitylene^b		3.90	2.18	3.90	2.18	3.90	2.18
Dinitromesitylene		7.17	1.32	7.17	1.79	0.87	1.79
Dinitrodurene^a		6.98	0.25	0.25	6.98	0.25	0.25
Dinitroisodurene		8.68	0.66^c	8.68	1.01	0.33^c	1.01
Aminodinitromesitylene Trinitromesitylene		8.81	0.59	8.81	0.96	...^{d}	0.96
Nitromesitylene		15.95	1.10	0.87	1.76	0.87	1.10
Aminonitromesitylene Dinitromesitylene		18.23	0.66	...^{d}	1.08	0.66	0.66
Nitrodurene^a		19.13	0.50	0.25	0.95	0.25	0.50
Diaminonitromesitylene Aminodinitromesitylene Trinitromesitylene		19.98	0.32	...^{d}	0.64	...^{d}	0.32
Pentamethylnitrobenzene		20.00	...^{d}	...	...	...	...
Aminonitroisodurene Dinitroisodurene		20.06	...^{d}	...	...	...	...
Aminonitrodurene Dinitrodurene		20.65	...^{d}	...	...	...	...
Diaminodurene Aminonitrodurene Dinitrodurene		4.65 (N) 5.09 (H)	1.55	1.55	4.65 (N) 5.09 (H)	1.55	1.55

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[a] Data from ref 30. [b] Data from ref 24. [c] Splittings cannot be assigned on experimental evidence alone and valence theory arguments have been used where necessary. [d] No splitting observed.

infra) these amino nitrogen and proton splittings are expected to be less than 150 mgauss and thus not resolvable. Reducing at −1.5 v gave an orange solution which exhibited a weak asymmetric esr signal consisting of 28 broad lines extending over 35 gauss which has not been interpreted. More cathodic than −1.9 v, the solution was still orange, but the spectrum obtained was strong and identical with that observed by Bernal and Fraenkel[5] on reduction at the third polarographic wave of trinitromesitylene; the spectrum was also identical with that of the diaminonitromesitylene anion.

Diaminonitromesitylene. Reduction at −1.5 v gave a yellow solution and an esr spectrum with 150-mgauss line widths. The interpretation of the proton hyperfine splittings was unambiguous, again assuming that no amino group splittings were observed. Under conditions of high gain, satellite lines assignable to splitting from ^{13}C and ^{15}N nuclei were observed. The intensity of the ^{13}C lines was approximately 0.73% of that of the major lines. Splitting from a ^{13}C nucleus at one of two equivalent positions is expected to give lines 1.10% of the major line intensity. Since the lines were somewhat overlapped, this is consistent with splitting from a ^{13}C nucleus at one of the three pairs of equivalent positions in the molecule. The ^{15}N satellites of the central ^{14}N line had intensities 0.2% of the major line intensities. Naturally occurring ^{15}N in the nitro group would be expected to give a splitting of 28.1 gauss and lines of intensity 0.55% of the ^{14}N lines. The ^{13}C and ^{15}N splittings were 8.07 ± 0.05 and 27.6 ± 0.2 gauss, respectively.

Dinitromesitylene. Reduction at −1.2 v gave a purple solution which displayed an esr signal similar to that previously reported.[5,27] Improved resolution allowed interpretationof the proton hyperfine structure. Reduction at −1.3 v gave a brown solution which displayed a weak asymmetric esr signal with 29 broad lines extending over 44 gauss which has not been interpreted. At potentials more negative than −1.5 v, an orange solution resulted which gave a strong esr spectrum identical with that reported by Bernal and Fraenkel, and to that of the aminonitromesitylene anion.

Aminonitromesitylene. Reduction at −1.4 v gave a pink solution exhibiting an esr spectrum with line widths of 200 mgauss. Because of the broad lines and small splittings, this spectrum could not be uniquely interpreted as first recorded. The lines were artificially sharpened by recording a mixture of the first and third derivative using the field modulation method of Glarum.[22] Lines 30% narrower than natural were obtained, allowing an unambiguous interpretation, but no splittings assignable to the amino group were observed.

Nitromesitylene. Reduction at −1.3 v gave a red solution exhibiting an esr spectrum with 150-mgauss line widths. The spectrum was qualitatively similar to that previously reported.[5,27] The interpretation of the proton hyperfine structure was unambiguous.

Dinitroisodurene (4,6-Dinitro-1,2,3,5-tetramethylbenzene). Reduction at −1.4 v gave a purple solution and an esr spectrum displaying the alternating line-width effect; the sharpest lines were about 175 mgauss wide. The interpretation of proton hyperfine structure was straightforward, but the methyl protons at the 2 and 5 positions were assigned by analogy to dinitromesitylene. Electrolysis at −1.8 v gave a brown solution exhibiting a weak asymmetric esr spectrum with 33 broad lines extending over 35 gauss which has not been interpreted. At potentials more negative than −2.0 v, the solution was orange and the spectrum obtained was identical with that of the aminonitroisodurene anion.

Aminonitroisodurene (4-Amino-6-nitro-1,2,3,5-tetramethylbenzene). Reduction at −1.9 v gave an orange solution with line widths of 100 mgauss. Each of the three nitrogen lines was split by several partially resolved 0.15-gauss splittings. Since the resolution was not sufficient for intensity measurements, this additional hyperfine structure could not be interpreted.

Dinitrodurene (3,6-Dinitro-1,2,4,5-tetramethylbenzene). Reducing at −1.2 v gave a yellow solution which displayed an esr signal identical with that previously reported.[5,25,27] The single dc polarographic wave given by dinitrodurene apparently corresponds to a two-electron reduction.[27] A plot of ϵ *vs.* log $(i_d - i)/i$ gives a straight line with a slope of 34 mv at 25°. At lower reduction potentials, however, no new radicals were formed, nor was the intensity of the dinitrodurene spectrum significantly diminished. When the DMF solution was made 1–2 m*M* in perchloric acid, the solution on reduction more cathodic than −1.5 v was red, and the esr spectrum obtained was identical with that reported by Bernal and Fraenkel and with that of the aminonitrodurene anion.[28] When the solution was made more acidic, approximately 5 m*M* in perchloric acid, the spectrum obtained was identical with that of the diaminodurene cation.

Aminonitrodurene (3-Amino-6-nitro-1,2,4,5-tetramethylbenzene). Reduction at −1.5 v gave a yellow solution exhibiting an esr spectrum with line widths of 800 mgauss. No proton or amino nitrogen splittings were resolved, and they are assumed to contribute to the observed line width. Each ^{14}N line had satellite lines, forming a 7.96 ± 0.05 gauss doublet. The best resolved satellite line had a derivative amplitude 1.0% of that of the major lines, and so can be assigned to a ^{13}C nucleus at one of the four pairs of equivalent sites in the molecule. The central line in the spectrum had an additional doublet splitting of 29.0 ± 0.2 gauss, with a derivative amplitude of 0.5% of this line; this splitting is assigned to a ^{15}N nucleus in the nitro group. These splittings are similar to those reported by Geske, *et al.*, for the anion of nitrodurene.[27]

Diaminodurene (3,6-Diamino-1,2,4,5-tetramethylbenzene). Oxidation at 0.7 v gave a yellow solution exhibiting an esr spectrum with 60-mgauss line widths. The assignment of hyperfine splittings was unambiguous and the values are similar to those reported by Das and Fraenkel[29] for the radical produced in dimethoxyethane solution.

Pentamethylnitrobenzene. Reduction at −1.6 v gave a red solution and an esr spectrum with 1.1-

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[27] D. H. Geske, J. L. Ragle, M. A. Bambenek, and A. L. Balch, *J. Am. Chem. Soc.*, **86**, 987 (1964).

[28] Geske, *et al.*,[27] reported an unidentified radical in acetonitrile solution which gave a single nitrogen splitting of 21.6 gauss, a line width of 0.7 gauss, and which arose from the dinitrodurene anion. Comparison with the present data suggests that this too was the aminonitrodurene anion.

[29] M. R. Das and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 792 (1965).

gauss line widths. The nitrogen splitting was similar to that observed previously.[27] No proton hyperfine splittings were resolved, presumably accounting for the broad lines. ^{13}C and ^{15}N satellite lines were observed. The lines assigned to splitting from ^{13}C had a derivative amplitude 0.8% of that of the major lines, consistent with splitting from a ^{13}C nucleus at one of the four pairs of equivalent positions in the molecule. The ^{13}C and ^{15}N splittings were 7.84 ± 0.05 and 28.0 ± 0.2 gauss, respectively.

***m*-Nitroaniline.** Reducing at −1.3 v gave an orange solution exhibiting an esr spectrum with 60-mgauss line widths. Even with relatively narrow lines, only about 150 of the expected 432 lines were well resolved. The spectrum is composed of ten distinct groups of lines. The outer groups of lines may be unambiguously interpreted as due to splittings from a single proton, two equivalent protons, and a nitrogen. Comparison of the various groups of lines yields another three proton splittings and a large nitrogen splitting. The splitting from the two equivalent protons and the smaller nitrogen splitting were assigned to the amino group, the large nitrogen splitting was assigned to the nitro group, and the remaining four proton splittings were assigned to specific ring positions by use of molecular orbital calculations and by analogy with nitrobenzene.[30]

***p*-Nitroaniline.** Reducing at −1.4 v gave a yellow solution exhibiting an esr spectrum with 100-mgauss line widths. The assignment of the amino proton splittings was determined by deuteration. The results are in good agreement with those recently reported by Fritsch, *et al.*[31]

***m*-Dinitrobenzene.** Reducing at −1.2 v gave an orange solution exhibiting an esr spectrum with 200-mgauss line widths, identical with that previously reported.[30,32] Reduction at potentials more negative than −2.2 v gave a weak spectrum of the *m*-nitroaniline anion. The intensity of this spectrum could be increased by the addition of small amounts of perchloric acid.

***p*-Dinitrobenzene.** Reducing at −1.1 v gave an orange solution exhibiting an esr spectrum with line widths of 100 mgauss, identical with that previously reported.[33] In pure DMF, no new radicals were detected, nor was the intensity of the spectrum diminished by electrolysis at potentials as negative as −2.6 v.[33] No new radicals could be detected in electrolyzed solutions made acidic with perchloric acid.

Discussion

Reduction Intermediates. All compounds studied were reduced to radical anions by electrolysis at potentials slightly more cathodic than the first half-wave potentials. At somewhat more negative potentials, but less cathodic than the potential of the second dc polarographic wave, di- and trinitromesitylene, dinitroaminomesitylene, and dinitroisodurene solutions change color to brown, and a new group of radicals are formed in poor yield. The spectra obtained have broad lines and are weak and unsymmetrical, indicating a mixture of paramagnetic species. In these four cases, the second half-wave potential of the starting material is more negative than the first half-wave potential of the amine to be formed, and reduction at, or more cathodic than the second half-wave potential invariably produced in aminonitro radical anion. The unidentified radicals must thus arise from reduction of products of reactions of the monoanions.

A clue to a possible mechanism is the report by Glarum and Marshall[24] that the trinitrotoluene anion radical is converted to a dianion radical by reduction 0.4 v more cathodic than the potential required to form the monoanion.[34] Because of steric effects, the nitromesitylenes are expected to be weaker acids than trinitrotoluene, so that it is not surprising that the corresponding dianion radicals are not observed in this work. Nonetheless, acid ionization is probably involved in the reduction scheme.

Diamagnetic brown solutions, similar in appearance to the solutions containing the unidentified radicals are obtained by the addition of base to the unreduced solutions of the dinitromesitylenes. In the case of dinitrodurene, which is expected to be a much weaker acid, and *m*-dinitrobenzene, which of course is not acidic, neither the brown color nor the intermediate radicals were observed. Neither of these underwent appreciable further reduction in the absence of an additional proton source. These observations suggest that the initial steps in the reduction of a nitro group in the dinitromesitylenes involve proton transfer from an activated methyl group to a nitro group, leaving a carbanion and a neutral radical. The addition of a second electron, and probably a second proton, to the radical is no doubt rapid, and, after elimination of water, would result in a nitroso group. The nitroso group is known to couple to an activated methyl group to give a substituted hydroxylamine, which, under some conditions, may rearrange to give nitrones, azoxy compounds, amides, or imines.[35,36] It has recently been shown that the anion radical of nitrosobenzene dimerizes to give azoxybenzene.[37] It is likely that the unidentified radicals are the one-electron reduction products of such compounds.

At more cathodic potentials, further electron transfer to the nitroso intermediates presumably competes effectively with the rates of the intermolecular coupling reactions, thus producing the observed amino compounds.

Dinitrodurene. The reduction of dinitrodurene differs from that of the dinitromesitylenes in a number of respects. The failure to observe unidentified radical intermediates was discussed above. The apparent two-electron wave is not presently understood, and preliminary work on electron-transfer kinetics indicates that the process is significantly irreversible. In addition, the appearance of the diaminodurene cation radical is of some interest since it appears as a stable

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(30) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, 39, 609 (1963).

(31) J. M. Fritsch, T. P. Layloff, and R. N. Adams, *J. Am. Chem. Soc.*, 87, 1312 (1965).

(32) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, 41, 699 (1964).

(33) Adams[8] has observed the formation of *p*-nitrophenol on prolonged electrolysis of *p*-dinitrobenzene in commercial DMF. We have been able to reproduce this result by making the solution basic with tetra-*n*-propylammonium hydroxide.

(34) We have found the monoanion radical of trinitrotoluene to be very unstable compared to the dianion under the same conditions. This instability is no doubt due to reactions similar to those discussed below.

(35) F. Krohnke, *Ber.*, 71, 2583 (1938).

(36) I. Tanasescu and I. Nanu, *ibid.*, 75, 1287 (1942).

(37) G. A. Russell and E. J. Geels, *J. Am. Chem. Soc.*, 87, 122 (1965).

intermediate in a solution being reduced at a potential nearly 2 v more negative than the reduction potential of the diaminodurene cation. The presence of small amounts of acid is expected to make this intermediate even more susceptible to reduction than indicated by the half-wave potential in DMF.[38]

Under the experimental conditions employed in this work, the radical product was observed to depend critically on the acid concentration. When the initial proton concentration was approximately the same as that of the dinitrodurene, the radical product was the aminonitrodurene anion, while higher initial proton concentrations gave the diaminodurene cation. The best resolved esr spectrum of this cation was obtained after relatively short reduction times. On prolonged electrolysis, the spectral lines were broadened, suggesting the presence of diaminodurene, which may undergo electron exchange with the cation, thus broadening the lines.

Neglecting possible dimerization or rearrangement reactions, the reduction of a nitro group in acidic solution may be pictured as going through the following intermediates.

$$\mathrm{RNO_2} \xrightarrow[\mathrm{H^+}]{\mathrm{e^-}} \mathrm{RNO_2H\cdot} \xrightarrow[\mathrm{H^+}]{\mathrm{e^-}} \mathrm{RNO} \xrightarrow[\mathrm{H^+}]{\mathrm{e^-}} \mathrm{RNOH\cdot}$$

$$\mathrm{RNOH\cdot} \xrightarrow[\mathrm{H^+}]{\mathrm{e^-}} \mathrm{RNHOH} \xrightarrow[\mathrm{2H^+}]{\mathrm{e^-}} \mathrm{RNH_2\cdot^+} \xrightarrow[\mathrm{H^+}]{\mathrm{e^-}} \mathrm{RNH_2^+}$$

The second and fourth electron transfers (to neutral radicals) are expected to be rapid at the potential required to make the first transfer rapid.[39] The nitroso group is reduced more easily than is the nitro group,[40] and the amine cation radicals are very easily reduced to amines (see Table I). Thus, of the expected intermediates, only the hydroxylamine is expected to have an appreciable lifetime in an acidic medium. Indeed, in aqueous alcohol, nitrobenzene shows a four-electron polarographic wave yielding phenylhydroxylamine, which in acidic solution shows a two-electron wave about 0.5 v more cathodic.[41]

In the present experiments, reduction of the first nitro group probably goes to the amine quite rapidly since all intermediates would retain an efficient electron acceptor, the second nitro group. During reduction of the second nitro group, however, at least some aminodurylhydroxylamine might escape from the electrode surface. This species might be expected to lose water to form duroquinonediimine which can undergo an electron-transfer reaction with diaminodurene to form two molecules of the diaminodurene cation radical. A similar mechanism has been proposed for the oxidation of *p*-phenylenediamine.[38]

Spin-Density Distributions. Two methods for estimating spin densities have been commonly employed in studies of π-electron radicals: straightforward calculation by valence theory methods and use of σ–π parameters to obtain spin densities from experimental nuclear hyperfine splittings. In the present examples, a number of problems arise which make both these methods somewhat questionable. In a valence theory calculation, nitro, methyl, and amino groups must be treated, as well as the effects of steric hindrance. σ–π parameters may also be altered by steric effects, and the constancy of these parameters is, in any case, somewhat uncertain. We shall therefore attempt to examine the data in a manner which minimizes reliance on explicit parameter values.

Rieger and Fraenkel[30] noted that Hückel MO theory predicts that the atomic orbital coefficients for the positions *ortho* and *para* to an electron-withdrawing substituent on a benzene ring are related to the energy of the molecular orbital by

$$c_o/c_p = (x^2 - 2)/2 \tag{1}$$

where x is the energy of the molecular orbital in units of β, the carbon–carbon resonance integral. If we accept the usual relation between splitting constant and spin density

$$a^{\mathrm{H}} = Q_{\mathrm{CH}}{}^{\mathrm{H}}\rho_{\mathrm{C}}{}^{\pi} \tag{2}$$

where a^{H} is the splitting constant of a ring proton, $\rho_{\mathrm{C}}{}^{\pi}$ is the π-electron spin density on the adjacent ring carbon atom, and $Q_{\mathrm{CH}}{}^{\mathrm{H}}$ is the σ–π parameter, we have, in the Hückel approximation

$$\pm(a_o{}^{\mathrm{H}}/a_p{}^{\mathrm{H}})^{1/2} = (x^2 - 2)/2 \tag{3}$$

The splitting of methyl protons is frequently assumed to follow a relation similar to eq 2

$$a^{\mathrm{H}} = Q_{\mathrm{CCH_3}}{}^{\mathrm{H}}\rho_{\mathrm{C}}{}^{\pi} \tag{4}$$

where $\rho_{\mathrm{C}}{}^{\pi}$ is again the π-electron spin density on the ring carbon atom. The applicability of eq 3 for the mononitro compounds considered here thus depends upon the validity of eq 1, and of eq 2 or 4, and upon the constancy of the σ–π parameters within a given molecule, but not upon their numerical values.

The observed increase in the nitrogen hyperfine splitting as the positions adjacent to the nitro group are substituted by bulky groups has been attributed to localization of the spin density on the nitro group as it is rotated out of the plane of the ring.[27] As the π-electron system of the nitro group becomes increasingly isolated from that of the benzene ring owing to this sterically enforced rotation, Hückel MO theory predicts that the energy of the first normally unoccupied molecular orbital should increase, approaching that of a nitro group in a nitro aliphatic molecule. The *ortho–para* splitting constant ratio is thus expected to decrease as the nitrogen splitting constant increases. Indeed, reference to Table III shows that a qualitative correlation exists between the *ortho–para* splitting constant ratio and the nitrogen splitting.

In a symmetrical 1,3-dinitro anion, Hückel theory predicts a node at the 2,5 positions. Rieger and Fraenkel[30] showed that the spin-density distribution in *m*-dinitrobenzene could not be adequately described by such a model. This failure was attributed to removal of the plane of symmetry by rapid exchange between two forms of the radical in which the unpaired electron was instantaneously isolated on one nitro group.[42] Dynamic frequency shift measurements[43] on the 1,3-dinitro anions discussed in this work have con-

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[38] H. Lee and R. N. Adams, *Anal. Chem.*, **34**, 1587 (1962).

[39] G. J. Hoijtink, J. van Schooten, E. de Boer, and W. I. Aalbersberg, *Rec. Trav. Chim.*, 73, 355 (1955).

[40] The half-wave potential of nitrosobenzene in DMF is −0.82 v *vs.* sce; R. D. Allendoerfer, unpublished observation.

[41] J. Pearson, *Trans. Faraday Soc.*, **44**, 683 (1948).

[42] J. H. Freed, P. H. Rieger, and G. K. Fraenkel, *J. Chem. Phys.*, 37, 1881 (1962).

[43] G. K. Fraenkel, *ibid.*, **42**, 4275 (1965).

Table III. Splitting Constant Ratios

Anion radical	a^N, gauss	a_o^H/a_p^H	$\mathcal{E}_{1/2}$, v	Q_o/Q_p
Nitrobenzene	9.70[a]	0.83[a]	−1.08	1.00
p-Nitrotoluene	10.06[b]	0.84[b]	−1.14[c]	1.03
3,5-Dimethylnitrobenzene	10.60[c]	0.82[c]	−1.13[c]	1.00
Nitromesitylene	15.95	0.63	−1.38	0.83
2,6-Dimethylnitrobenzene	16.47[a]	0.64[a]	−1.34[c]	0.84
Nitrodurene	19.13[a]	0.53[a]	−1.44[d]	0.72
Diaminonitromesitylene	19.98	0.50	−1.49	0.70
Dinitromesitylene	7.17	0.59[e]	−1.15	
Dinitroisodurene	8.68	0.49[e]	−1.18	
Dinitroaminomesitylene	8.81	0.44[e]	−1.23	

[a] Data from ref 29. [b] Data from ref 30. [c] Data from ref 27; solvent acetonitrile; solvent effect correction $\mathcal{E}_{1/2}$(DMF) − $\mathcal{E}_{1/2}$(MeCN) = 0.062 v. [d] D. H. Geske, private communication. [e] $a_2^H/(2a_4^H - a_2^H)$.

firmed the two-jump model, at least for these examples.[44] Assuming that this model gives an accurate description of the instantaneous spin-density distribution, the observed distribution should be the average of the distributions in the two instantaneous forms.[45] For a 1,3-dinitro anion, the spin densities at positions 2 and 4 are thus related to the spin densities at the corresponding positions in the contributing forms. Thus $a_2^H = a_o^H$ and $a_4^H = (a_o^H + a_p^H)/2$ where a_o^H and a_p^H are the splittings in the contributing radicals at the positions *ortho* and *para* to the charged nitro group, respectively. Substituents *meta* to a highly charged nitro group may be shown (*vide infra*) to have little effect on the spin-density distribution in the molecule; thus, we expect the distribution in the contributing forms to be similar to that of the hindered mononitro radicals studied in this work. If this is the case, then the ratio $a_2^H/(2a_4^H - a_2^H)$ should be a measure of the energy of the odd electron in the instantaneous radical. This ratio is identically zero in the simple Hückel theory model. The computed values of the ratio are given in Table III for dinitromesitylene, dinitroisodurene, and dinitroaminomesitylene, and again a correlation with nitrogen splitting constants is observed. *m*-Dinitrobenzene, on the other hand, gives a ratio of 0.44 and a nitrogen splitting of 3.97 gauss,[30] suggesting that the two-jump model is only approximately correct in this case.

The similarity of the nitro nitrogen splittings for the diaminonitromesitylene, aminonitroisodurene, and pentamethylnitrobenzene anions, and also the similarity of the splittings from the aminodinitromesitylene and dinitroisodurene anions, suggest that the combination of inductive and steric effects of methyl and amino groups is very nearly the same when these groups are *meta* to a nitro group. At the *para* position, on the other hand, resonance interaction is apparently still possible, even with the nitro group appreciably twisted out of the plane of the ring. Thus the nitro nitrogen splitting of aminonitrodurene is significantly greater than that of the diaminonitromesitylene, aminonitroisodurene, or pentamethylnitrobenzene anions.

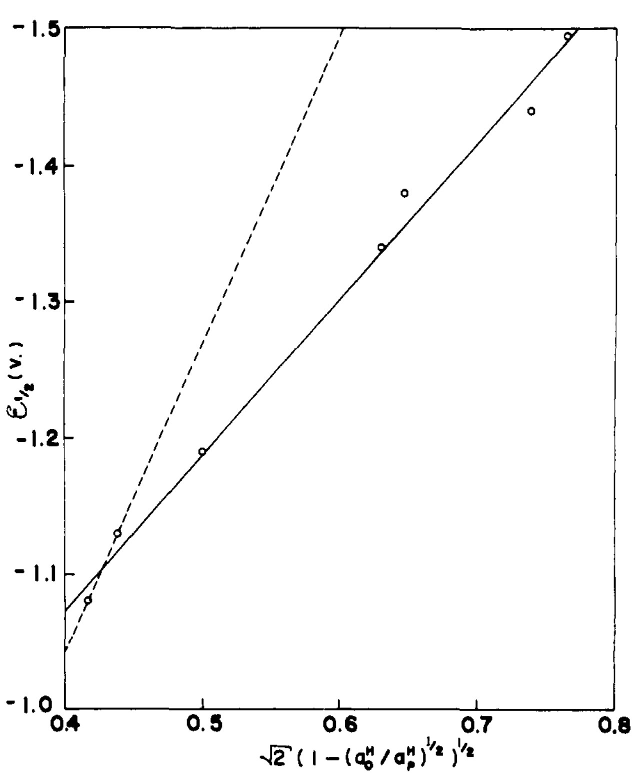

Figure 1. Plot of $\mathcal{E}_{1/2}$ *vs.* a function of the *ortho–para* splitting constant ratio. The dashed line corresponds to a slope of −2.28 ev.

Reversible one-electron polarographic half-wave potentials have been shown to correlate well with energies calculated by Hückel MO theory according to

$$\mathcal{E}_{1/2} = bx + c \tag{5}$$

where b and c are empirical parameters.[46] Equations 3 and 5 may be combined to predict a linear relation between half-wave potentials and a function of the splitting constant ratio

$$\mathcal{E}_{1/2} = 2^{1/2}b\,[1 - (a_o^H/a_p^H)]^{1/2} + c \tag{6}$$

Equation 6 is plotted for six mononitro radical anions in Figure 1. An approximate straight line is indeed obtained, with least-squares parameters $b = -1.14 \pm 0.05$ ev, and $c = -0.62 \pm 0.07$ v. The value of b is about half that usually obtained from correlation of polarographic data with Hückel energies.[46]

This deviation might arise from errors in interpretation or derivation of eq 3 and 5, and these are examined below. In the gas phase, the Hückel approximation equates the energy of the first unfilled molecular orbital x with the electron affinity of the neutral molecule. Thus, neglecting entropy effects, the gas-phase polarographic half-wave potential is proportional to this energy with a proportionality constant β. The customary use of constant parameters in Hückel calculations is equivalent to neglect of environmental effects and may lead to lack of charge self-consistency. Thus in solution, the change in the free energy of solvation $\Delta\Delta F_s$ must also be accounted for. In general, $\Delta\Delta F_s$ will not be constant for a given series of anions. As the delocalization of the unpaired electron increases, $\Delta\Delta F_s$ is expected to decrease, and it has been suggested[46] that the variation in $\Delta\Delta F_s$ is proportional to x. If this proportionality constant is k, then the relation of $\mathcal{E}_{1/2}$ to x

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(44) R. D. Allendoerfer and P. H. Rieger, to be published.

(45) This is equivalent to the valence-bond superposition approximation; see J. C. Schug, T. H. Brown, and M. Karplus, *J. Chem. Phys.*, 37, 330 (1962).

(46) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 173 ff.

may be written

$$\mathcal{E}_{1/2} = (1 + k)\beta x + c \qquad (7)$$

Thus b in eq 5 is $(1 + k)\beta$. This interpretation should apply to the value of $b = -2.28$ ev found by Rieger and Fraenkel,[30] though there is no way of evaluating k.

For the present system in contrast to the one above, x is an experimental quantity determined from the esr spectrum and eq 3 and thus presumably includes the effects of solvation. Rieger and Fraenkel[30] have shown that the variation in splitting constants with solvent can be treated by varying the MO parameters and thus x. Hückel MO calculations, including the McLachlan[47] procedure for approximately introducing configuration interaction, for the nitrobenzene anion can fit the *ortho-para* splitting constant ratio exactly, using parameters similar to those employed by Rieger and Fraenkel.[30] The best fit to the experimental spin densities, obtained by using $Q_{CH}^{H} = -27.0$ gauss, was produced by the following parameters: $h_O = 1.50$, $h_N = 2.01$, $k_{CN} = 1.04$, $k_{NO} = 1.62$. The *ortho-para* splitting constant ratio for hindered nitrobenzenes can be estimated in the limiting case of no π-electron interaction with the benzene ring by a calculation on an isolated nitro group and the application of eq 3. Any reasonable set of nitro parameters which fits nitrobenzene yields a limiting ratio of about 0.70. On the other hand, the half-wave potential of 2-methyl-2-nitropropane, where no π-electron interaction is possible, is -1.70 v,[27] and this, together with Figure 1, suggests that the limiting ratio should be about 0.37. This estimate is in much better agreement with the lowest experimental value of 0.5. The solvation energies of hindered and unhindered nitrobenzene anions are most certainly different, and thus we have a clear example of the breakdown of a Hückel theory prediction, caused by the use of constant parameters to describe different chemical environments.

Since these solvent effects are here included in the experimental x, the value of b obtained from Figure 1 should be solvent independent and thus a measure of β only. Thus, a value of k of about 1 for the Rieger and Fraenkel[30] data would explain the observed deviation in b's and give a value of β similar to that determined from thermodynamic considerations.[46] However, the values of b determined for aromatic hydrocarbons in various solvents[46] are all close to the Rieger and Fraenkel value which suggests that k is either small compared to 1 or surprisingly constant for the wide range of compounds studied.

Examining other possible sources of error, we note that eq 1, when used in this way, is by definition self-consistent. Inclusion of configuration interaction in an MO calculation decreases the predicted *ortho-para* ratio slightly, but this contribution is approximately constant in the present context and can justifiably be neglected. Another explanation for the observed deviation is an error in eq 2 or 4 leading to an incorrect evaluation of x from eq 3. Q_{CH}^{H} is expected to be a function of net charge,[48] and possibly of spin density on neighboring atoms,[49] but these effects are not expected to be important in those molecules for which this parameter was used.

Inasmuch as the points for 2,6-dimethylnitrobenzene and nitrodurene fall on the same line as those for which the *ortho* and *para* substituents are identical, it appears that the parameters Q_{CH}^{H} and $Q_{CCH_3}^{H}$ are nearly identical, at least at the *para* position.[50] The *ortho* substituents, on the other hand, are methyl groups for the four points on the right side of Figure 1 and hydrogens for the two left-hand points. Thus a systematic deviation of $Q_{CCH_3}^{H}$ for *o*-methyl groups would result in a change in slope rather than scatter of points. If we adopt a larger value of b, and a modified version of eq 6, the parameter $Q_{CCH_3}^{H}$ must decrease with increasing steric hindrance. The ratio Q_o/Q_p required to fit the points to a straight line passing through the nitrobenzene point and with an arbitrary slope of -2.28 ev, the dashed line of Figure 1, is given for the various radicals in Table III.

One can conceive of two ways in which steric hindrance between the nitro and methyl groups might affect $Q_{CCH_3}^{H}$. The X-ray structure of nitromesitylene[51] indicates that the nine carbon atoms and the nitrogen atom are very nearly coplanar, and that the nitro group is inclined at an angle of about 66° with respect to the ring. In the anion radical, however, the carbon–nitrogen bond order is expected to increase significantly, so that the angle of the nitro group should be less, and the distortion of the carbon skeleton might be considerably greater. Thus, if the methyl groups are (on the average) pushed out of the plane of the ring, overlap between the appropriate methyl group orbitals[52] and the π system of the ring is expected to decrease, thus reducing the π-electron delocalization on the methyl group. This effect may be related to similar observations on proton splittings in formyl and acetyl groups. In these cases, the acetyl methyl proton splitting was roughly half to three-quarters of the formyl proton splitting in otherwise identical radicals.[53] Although some changes in spin density must occur as a result of steric effects on the planarity of the π system, the ring splitting constant changes are small, suggesting that the large difference between the formyl and acetyl proton splittings may be due in part to steric effects on $Q_{CCH_3}^{H}$.

A second mechanism for the apparent reduction of $Q_{CCH_3}^{H}$ would involve hydrogen bonding or some other direct interaction of the methyl protons with the nitro group. Such an interaction might lead to a splitting contribution of sign opposite to that of the "normal" contribution, resulting in a decrease in the total splitting. With the data at hand, however, this mechanism is difficult to evaluate.

Carbon-13 Splittings. The ^{13}C lines observed in the spectra of pentamethylnitrobenzene, aminonitrodurene, and diaminonitromesitylene have the intensity expected for a ^{13}C nucleus at one of the pairs of equivalent carbon positions. Thus the splitting may be assigned to the 2,6 or 3,5 ring positions or to the methyl carbon

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(47) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(48) J. R. Bolton, *J. Chem. Phys.*, **43**, 309 (1965).

(49) G. Giacometti, P. L. Nordio, and M. V. Pavan, *Theoret. Chim. Acta*, **1**, 404 (1963).

(50) Assuming similar spin-density distributions, the splitting constants of the nitrobenzene[20] and *p*-nitrotoluene[31] anions suggest that Q_{CH}^{H} and $Q_{CCH_3}^{H}$ are equal to within a few per cent.

(51) J. Trotter, *Acta Cryst.*, **12**, 605 (1959).

(52) D. B. Chesnut, *J. Chem. Phys.*, **29**, 43 (1958).

(53) P. H. Rieger and G. K. Fraenkel, *ibid.*, **37**, 2811 (1962); N. Steinberger and G. K. Fraenkel, *ibid.*, **40**, 723 (1964).

atoms at the 2,6 positions. The splittings, 7.84, 7.96, and 8.07 gauss, respectively, are very similar to splittings reported by Geske, *et al.*, for the anions of pentamethylnitrobenzene (8.4 gauss),[54] nitrodurene (7.6 gauss),[27] 2,4,6-tri-*t*-butylnitrobenzene (9.4 gauss),[54] 2,6-tri-*t*-butyl-4-amino-nitrobenzene (9.8 gauss),[27] and 2,3,5,6-tetraisopropylnitrobenzene (9.3 and 7.7 gauss).[54,55] Since the spin density at the 3,5 positions (*meta* to the nitro group) is undoubtedly very small, it is probable that the splitting arises from the ring carbon atoms or the methyl (or isopropyl or *t*-butyl) carbon atoms at the 2,6 positions. As has been pointed out by Geske,[27] the procedure of Karplus and Fraenkel[56] is incapable of explaining a splitting of more than about 1 gauss at the ring carbon atoms, even for rather generous estimates of spin densities. The methyl carbon splitting would be expected to be even less.[57]

A number of unusual mechanisms for the origin of this splitting can be imagined. If the methyl groups *ortho* to the nitro group are pushed out of the plane of the ring, as suggested above, it is conceivable that the parameter $Q_{CC'}{}^{C}$ would increase sufficiently through rehybridization of the ring carbon atom to account for the observed splitting. However, studies of orbital following have suggested that rehybridization occurs only to a very limited degree.[58] Similarly, as the methyl group is moved above or below the plane of the ring, some degree of overlap of the methyl carbon 2s orbital with the π system is expected to occur. Sample calculations of this effect, however, indicate that the expected splitting is far smaller than that observed. Estimates of the splitting due to nitrogen and oxygen π-orbital density at the methyl and ring carbon nuclei are likewise far smaller than the observed splittings.

The most probable mechanism of the splitting, and also the most difficult to estimate quantitatively, involves delocalization of the unpaired electron density from the "π" system of the nitro group into the "σ" system of the benzene ring. In these molecules, the nitrogen and oxygen 2p orbitals have appreciable overlap with the $2p_x$ orbitals of the ring carbon atoms at positions 1 and 2,6. Very crude estimates suggest that such a resonance interaction is responsible for the observed splittings. A fuller study of this interaction is of some interest, but should be postponed until an experimental basis for the assignment is available.

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(54) T. M. McKinney and D. H. Geske, *J. Chem. Phys.*, **44**, 2277 (1966).

(55) Two conformational isomers; see ref 54.

(56) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

(57) H. L. Strauss and G. K. Fraenkel, *ibid.*, **35**, 1738 (1961).

(58) D. M. Schrader and M. Karplus, *ibid.*, **40**, 1593 (1964).

Hydrogen Bonding in Thiols[1]

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Abstract: Dilution shifts of the sulfhydryl proton magnetic resonance signal have been used to obtain hydrogen-bonding association constants of several thiols. The dimerization constants (K_2) in M^{-1} of thiols in carbon tetrachloride are: ethyl, 0.0056; *n*-propyl, 0.011; isopropyl, 0.0126; *n*-butyl, 0.0132; *t*-butyl, 0.0067; cyclohexyl, 0.093. Since K_2 (= 0.0182) for 1-butanethiol in cyclohexane is close to K_2 in carbon tetrachloride, this suggests that at least for these solvents, no specific or peculiar medium effects on the thiols are present. Structural effects on the magnitude of K_2 are consistent with the known polar and steric effects of the groups involved. A comparison of our K_2 values with those previously determined indicates rough agreement. In carbon tetrachloride, our data for thiophenol indicated an apparent monomer–tetramer association ($K_4 = 10^{-4}\ M^{-3}$), but in chlorobenzene, the thiophenol data were consistent with a monomer–dimer equilibrium ($K_2 = 0.011\ M^{-1}$). Because the medium anisotropy in carbon tetrachloride changes drastically with thiophenol concentration, an effect which is largely absent in chlorobenzene, we believe that the existence of tetramer is illusory.

At one time, it was claimed that thiols do not self-associate through hydrogen bonds.[3] Evidence against such bonding was adduced through studies using such techniques as cryoscopy,[4] dipole moment,[5] solubility,[6] proton magnetic resonance (pmr),[7] and infrared spectroscopy.[8] As recently as 1958 at a conference whose theme was "Sulfur in Proteins," the possibility of S···H—S bonds could only be con-

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(2) National Science Foundation Fellow, 1961–1963.

(3) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

(4) E. N. Lassettre, *Chem. Rev.*, 20, 259 (1937).

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