

adsorption leading to an increase in the absolute value of the partial molal enthalpy of adsorption at the higher temperature. The lack of mobility at 150°K. does not allow the atoms to move under the attractive forces.

Figure 4 shows two sets of data for hydrogen adsorption at 280°K. on carbon-supported platinum. In the first run (closed circles) the partial molal enthalpies fell to a value less than 10 kcal./mole of H₂ at considerably less than monolayer coverages assuming all of the platinum exposed. It thus seems that not all the platinum atoms are exposed, *i.e.*, that there were patches on the surface with more than one layer of platinum atoms. In the second run made after the sample was saturated with oxygen, the values fell to less than 10 kcal./mole of H₂ only after the monolayer was reached. A redistribution of the platinum obviously has taken place, the platinum atoms having spread to form a complete monolayer. Although, as has already been pointed out, the carbon-supported platinum does not chemisorb oxygen, the addition of oxygen is in some way responsible for the change.

As for the platinum black, a markedly lower value for the enthalpy at the lower temperature is noted. There is one difference on the carbon-supported platinum; at 150°K. the enthalpies drop to values of physical adsorption at about $\theta = 0.45$.

The curve for the adsorption of oxygen on platinum black at 280°K. (Fig. 6) shows a slight maximum

in the measured enthalpies with increasing oxygen coverage. Since the measurements were made with a precision of about 1% and the second set of measurements fall within this precision, the maximum is probably real; however, there is certainly a point of inflection. The measurements at 200°K. show the same effect at about the same coverage. This effect suggests a cooperative process involving the adsorbed oxygen atoms. It has already been observed that the molal heat capacities of oxygen on bulk platinum are those of a hindered translator.¹³ Hindered translation can only mean a mobile monolayer. At low coverages, the oxygen must adsorb in clusters which, as the coverage increases, coalesce into larger patches with heat evolution thus accounting for the flattening of the curve. Eventually a complete oxygen atom network covers the surface with one oxygen atom per platinum atom.

At 77°K., the cooperative effect is not manifest in the results even though it is apparent that oxygen does chemisorb. In keeping with this, there is a definite difference in the type of adsorption at 77°K. Evidently the adsorbed oxygen atoms have become localized.

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The Cation Radical of Tetrakis(dimethylamino)ethylene

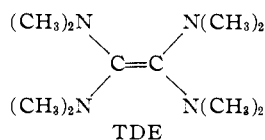
BY KEIJI KUWATA¹ AND DAVID H. GESKE

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Examination of the polarographic behavior of tetrakis(dimethylamino)ethylene (TDE) showed a two-step wave corresponding to oxidation to TDE⁺ and TDE⁺². The cation radical TDE⁺ was obtained by oxidation of TDE and reduction of TDE⁺² as well as by the homogeneous reaction of TDE and TDE⁺². The electron spin resonance spectrum of TDE⁺ was obtained. The assigned coupling constants are $a_N = 4.85 \pm 0.01$ (four equivalent N¹⁴ nuclei), $a_H = 2.84 \pm 0.01$ (twelve equivalent protons), $a_H = 3.28 \pm 0.01$ G. (twelve equivalent protons). The nitrogen coupling constant is discussed in relation to coupling constants for other nitrogenous cation radicals. Observation of two different methyl proton coupling constants is rationalized in terms of restricted rotation about the C-N(CH₃)₂ bond.

Introduction

Recent characterization of tetrakis(dimethylamino)ethylene (TDE) as a strong electron donor and the preparation of salts of the corresponding dication²



TDE⁺², strongly suggest that the paramagnetic monocation TDE⁺ should exist, at least as a transient species. The formal resemblance of TDE⁺ to the cation radical of N,N,N',N'-tetramethylphenylenediamine (Wurster's blue) is of considerable interest. We report here the electron spin resonance spectrum of the remarkably stable radical TDE⁺ as well as electrochemical parameters for the TDE system.^{2a}

(1) On leave from Osaka University, Osaka, Japan.

(2) N. Wiberg and J. W. Buchler, *Angew. Chem.*, **74**, 490 (1962); *Angew. Chem. Intern. Ed. Engl.*, **1**, 406 (1962); *Chem. Ber.*, **96**, 3223 (1963).

Experimental

Tetrakis(dimethylamino)ethylene, as prepared by the method of Pruett,³ *et al.*, was obtained from Chemical Intermediates and Research Laboratories, Cuyahoga Falls, Ohio. Since the compound is sensitive to moisture and oxygen, it was stored in a serum bottle and handled with a syringe. Tetrakis(dimethylamino)ethylene dibromide, TDE⁺²(Br⁻)₂, is precipitated when ether solutions of bromine and TDE are mixed.^{2,4} It may also be prepared by controlled potential electrooxidation of TDE at -0.1 v. *vs.* aqueous saturated calomel electrode (s.c.e.) in acetonitrile or dimethylformamide with 0.1 M tetraethylammonium bromide

(2a) NOTE ADDED IN PROOF.—The above authors² have informed us that they observed the orange color of TDE⁺ when alcoholic solutions of TDE were exposed to oxygen (J. W. Buchler, Doctoral Dissertation, University of Munich, 1963, p. 41). The mass spectrum of TDE obtained at an ionization voltage of 6.5 v. showed a small parent peak (mass 200). Above an ionization voltage of 9 v. fragmentation occurred. No TDE⁺² was formed by electron impact [N. Wiberg and J. W. Buchler, private communication; see also *Angew. Chem.*, **75**, 1112 (1963)].

(3) R. L. Pruett, K. E. Rapp, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *J. Am. Chem. Soc.*, **72**, 3646 (1950).

(4) Pruett, *et al.*,³ actually prepared this compound in 1950 and noted that the compound dissolved in water and that silver bromide was precipitated upon addition of silver nitrate. However, characterization as an ionic salt was not done.

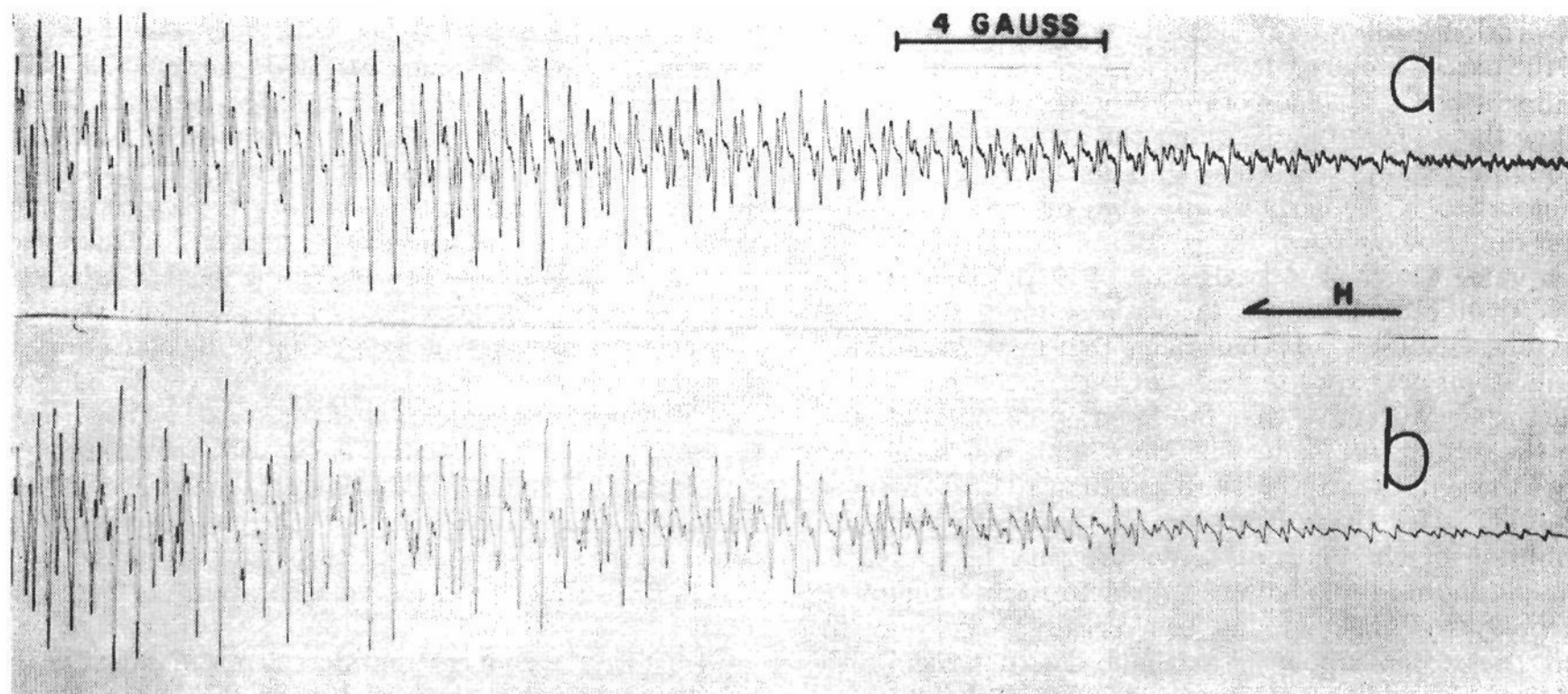


Fig. 1.—a, Derivative e.s.r. spectrum (low field one-half) of TDE^+ as obtained by reaction of $10^{-4} M$ TDE and $10^{-4} M$ $\text{TDE}^{+2}(\text{Br}^-)_2$ in dimethylformamide solution. b, Calculated spectrum using coupling constants given in text and line width of 0.05 G. (Lorentzian line shape).

present as supporting electrolyte. Under the latter conditions the m.p. for $\text{TDE}^{+2}(\text{Br}^-)_2$ was 263° , compared with the value of 252° noted by Wiberg and Buchler.² The compound prepared by electrooxidation of TDE showed 42.1% Br by gravimetric analysis as compared with the calculated value of 44.4%. $\text{TDE}^{+2}(\text{ClO}_4^-)_2$ was prepared by the same kind of electrooxidation but with tetraethylammonium perchlorate as supporting electrolyte. The decomposition point of the perchlorate is 279° .

Perdeuteriotetrakis(dimethylamino)ethylene was prepared as described by Pruett, *et al.*,³ with appropriate modification for a small-scale preparation. A mixture of 20 mmoles of deuterated dimethylamine⁵ and 2.5 mmoles of chlorotrifluoroethylene was sealed in a heavy wall glass tube. The temperature of the tube was increased from -80 to 60° over a period of 26 hr. and held at 60° for 5 hr. with moderate shaking. The reaction product, containing solid dimethylammonium fluoride and chloride, was fractionated under vacuum; 1.27 mmoles of perdeuterio-TDE was collected and further purified by conversion to the dibromide. The yield on basis of the dibromide was 51%.

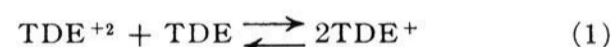
Acetonitrile and dimethylformamide were purified as described elsewhere.⁶ Tetraethylammonium perchlorate was prepared by neutralization of tetraethylammonium hydroxide and perchloric acid.

A Varian V-4502 X-band e.s.r. spectrometer with 100 kc. field modulation was used in conjunction with a Varian 12-in. magnet to secure the spectra presented here. When the radical cation was generated electrolytically a recirculation cell⁷ was used. Polarographic measurements were made at approximately 25° using the ORNL three electrode polarograph manufactured by Indiana Instrument and Chemical Corp., Bloomington, Ind.

Results and Discussion

Electrochemical Studies.—A preliminary polarographic investigation of the TDE system was undertaken as a guide to electrogeneration of the cation radical. A 0.43 mM solution of TDE in acetonitrile solution with 0.1 M tetraethylammonium perchlorate as supporting electrolyte undergoes a two-step oxidation at a dropping mercury electrode. The half-wave potentials are -0.75 and -0.61 v. *vs.* aq. s.c.e. and the diffusion current constant, $i_d/m^{2/3}t^{1/6}C$, for the over-all two-electron process is $3.6 \mu\text{a. mg.}^{-2/3} \text{ sec.}^{1/2} \text{ mM}^{-1}$. The remarkably negative potential at which TDE is

oxidized is quantitative evidence for its description as a "strong" electron donor.² In fact the half-wave potential corresponding to removal of the first electron from TDE is sufficiently negative to *add* an electron to *p*-dinitrobenzene. Reduction of a 0.35 mM acetonitrile solution of $\text{TDE}^{+2}(\text{ClO}_4^-)_2$ shows half-wave potentials of -0.61 and -0.75 v. *vs.* aq. s.c.e. with an over-all current constant of $4.7 \mu\text{a. mg.}^{-2/3} \text{ sec.}^{1/2} \text{ mM}^{-1}$. On basis of the stated half-wave potentials, the equilibrium constant for the reaction given in eq. 1 is estimated as 2.3×10^2 . For higher con-



centration of TDE and $\text{TDE}^{+2}(\text{ClO}_4^-)_2$ the individual polarographic waves were less well resolved, *i.e.*, the curves tended to coalesce. This effect is being investigated further.

Electron Spin Resonance Spectra.—Controlled potential electrolysis of acetonitrile or dimethylformamide solutions of TDE or $\text{TDE}^{+2}(\text{ClO}_4^-)_2$ at approximately -0.7 v. *vs.* s.c.e. yielded solutions with an intense absorption maximum at $385 \text{ m}\mu$ ⁸ which exhibited e.s.r. spectra comparable to that shown in Fig. 1a except that the lines were slightly broader. The e.s.r. spectrum⁹ of TDE^+ in dimethylformamide solution is shown in Fig. 1a. The radical was prepared by homogeneous reaction (eq. 1) of $10^{-4} M$ solutions of TDE and $\text{TDE}^{+2}(\text{Br}^-)_2$. Preparation of the solution with vacuum degassing appears to permit more complete removal of oxygen (as evidenced by the narrower e.s.r. lines) than was possible in the electrolysis experiments. For radical concentrations below $10^{-4} M$, the line widths are approximately 0.04 gauss (G.). The *g*-value is 2.0036 ± 0.0003 . In dimethylformamide solution the spectrum showed no variation in shape over the temperature range 0 to 120° .

Assignment of coupling constants to the spectrum in Fig. 1a was facilitated by examination of the e.s.r. spectrum for the corresponding perdeuterio cation

(5) This material was secured from Volk Radiochemical Co., Skokie, Ill. Mass spectrometric analysis showed dimethylamine- d_6 , 95.88%; dimethylamine- d_5 , 2.16%; and dimethylamine- d_4 , 1.96%.

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

(7) J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, **39**, 778 (1963).

(8) The dication TDE^{+2} has an absorption peak at $277 \text{ m}\mu$ with a molar absorptivity of 1.1×10^4 in acetonitrile.

(9) For clarity of presentation only the low-field one-half of the spectrum is shown. All the spectra observed have been symmetrical about the center.

$C_2N_4(CD_3)_8^+$ as obtained by electroreduction of $C_2N_4(CD_3)_8^{+2}(Br^-)_2$. From this spectrum,⁹ Fig. 2a, the major splitting of 4.92 ± 0.04 G. is readily assigned to four equivalent N^{14} nuclei. The deuteron splittings of 0.47 G. correspond to hydrogen coupling constants of approximately 3 G.; however, the *a priori* assignment of the number of deuterons involved in the coupling is not possible from this spectrum alone.¹⁰

Final assignment of the TDE⁺ spectrum was made with the following coupling constants: $a_N = 4.85 \pm 0.01$ (four equivalent N^{14} nuclei), $a_H = 3.28 \pm 0.01$ (twelve equivalent protons), $a_D = 2.84 \pm 0.01$ G. (twelve equivalent deuterons). The simulated spectrum in Fig. 1b was calculated and plotted at 0.01-G. intervals using the above constants and a line width of 0.05 G. The computer program employed here has been described previously.¹¹ Approximately 300 of the possible total of 1521 lines are observed in the experimental spectrum. Some of the small differences between the calculated and experimental spectra are due to splittings from carbon-13 present in natural abundance. For instance, lines originating from carbon-13 in the β -methyl groups are expected to be 2.2% as intense as the "parent" line.

An indication of the stability of TDE⁺ is afforded by the fact that the e.s.r. spectrum could be obtained at 120°. The radical is stable in dimethylformamide with up to 10% water present but it does react rapidly with oxygen. Thus TDE⁺ is an aliphatic radical comparable in stability to the anion radical of tetracyanoethylene.

Isotropic Nitrogen Coupling Constant.—Nitrogen coupling constants for several cation radicals related to TDE⁺ are presented in Table I. Melchior and

	a_N , G.	a_{H1} , G.	a_{H2} , G.
	5.29 ^a (5.12) ^b	2.13 (2.10)	5.88 (5.67)
	6.99 ^c	1.97	6.76
H_3N^+	19.5 ^d	25.9	
$(CH_3)_3N^+$	18.0 ^e	26.7	
	4.85	2.84	3.28

^a Data taken from ref. 12. ^b See ref. 13. ^c Data taken from ref. 14. ^d Data taken from ref. 17. ^e Data taken from ref. 18.

Maki¹² examined the e.s.r. spectrum of the cation radical¹³ of *p*-phenylenediamine, PDA⁺, and discussed the nature of coupling of the unpaired electron with the N^{14} nucleus. The two mechanisms considered

(10) Whereas two different kinds of proton coupling constants were observed in TDE⁺, it was not expected that two different deuteron coupling constants will be resolved in the perdeuterated radical since they would differ by only 0.07 G. The simulated spectrum, Fig. 2b, was constructed using deuteron coupling constants of 0.50 and 0.44 G., each for twelve equivalent deuterons, and a line width of 0.12 G.

(11) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **38**, 1999 (1963).

(12) M. T. Melchior and A. H. Maki, *ibid.*, **34**, 471 (1961).

(13) There is only a small solvent effect on this cation radical as demonstrated by the work of L. H. Piette, P. Ludwig, and R. N. Adams, *Anal. Chem.*, **34**, 916 (1962), who observed coupling constants as given in parentheses in Table I using an aqueous solution buffered at a pH of 4.8.

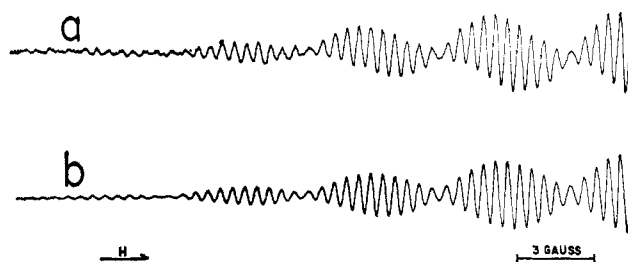


Fig. 2.—a, Derivative e.s.r. spectrum (low field one-half) obtained on electroreduction of 2.8×10^{-4} M acetonitrile solution of $C_2N_4(CD_3)_8^{+2}(Br^-)_2$. b, Calculated spectrum using coupling constants given in text and line width of 0.12 G. (Lorentzian line shape).

were (a) π - σ electronic exchange interaction on the carbon adjacent to the nitrogen with transmission of spin polarization into the C-N bond and (b) π - σ interaction on the nitrogen atom transmitting unpaired spin polarization into all three nitrogen σ -bonds. The magnitude of a_N relative to that of the amine protons was shown to be consistent with the latter mechanism.

Melchior and Maki¹² found that the nitrogen π -electron spin density, ρ_N^π , calculated by the Hückel molecular orbital (HMO) method was 0.236 and then suggested that the relationship

$$a_N = Q_N \rho_N^\pi \quad (2)$$

fitted the experimental data when Q_N was 22.4. They, however, cautioned that "the mechanism of nitrogen hyperfine interaction is probably too complex for such an expression."

The cation radical of N,N,N',N'-tetramethyl-*p*-phenylenediamine (Wurster's blue) has been studied extensively. The correct coupling constants as established by Bolton and co-workers¹⁴ are given in Table I. Rather surprisingly, the nitrogen coupling constant in Wurster's blue cation is 30% larger than in PDA⁺. In 1958, McLachlan¹⁵ presented HMO calculations for the Wurster's blue cation. The calculation for $\alpha_N = \alpha_C + \beta_{CC}$ and $\beta_{CC} = \beta_{CN}$ predicted a spin density of 0.078 on the four equivalent ring carbons, which when combined with the usual¹⁶ Q_N of 23.7 G. predicts a ring proton coupling constant of 1.85 G. in comparison with the observed value of 1.97 G. The calculated nitrogen spin density was 0.22, corresponding to a Q_N value of 31.8 G.

Both the H_3N^+ and $(CH_3)_3N^+$ radicals have been studied^{17,18}; see Table I. It is interesting that the nitrogen coupling constants of 19.5 and 18.0 G. in these radicals are of the same order as the Q_N values mentioned above.

Molecular orbital calculations for PDA⁺ and Wurster's blue cation offer the advantage that a successful calculation must first of all predict rather accurately the ring proton coupling constants, an independent condition not available in calculations for TDE⁺. Nevertheless, calculation of spin densities in TDE⁺ have been done using the HMO method. Assuming the radical to be coplanar and taking the nitrogen coulomb integral as $\alpha_N = \alpha_C + \sigma\beta_{CC}$ and letting

(14) J. R. Bolton, A. Carrington, and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 615 (1963).

(15) A. D. McLachlan, *ibid.*, **1**, 233 (1958).

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

(17) T. Cole, *ibid.*, **35**, 1169 (1961).

(18) A. J. Tench, *ibid.*, **38**, 593 (1963).

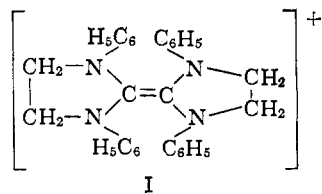
$\beta_{CN} = \beta_{CC}$, we find that the calculated nitrogen π -electron spin density changes from 0.167 to 0.125 as σ changes from 0 to 1.0. Correspondingly, the π -electron spin density of the ethylene carbon varies from 0.166 to 0.250. For comparison, the nitrogen π -electron spin density estimated from the experimental nitrogen coupling constant for TDE⁺ and eq. 2 taking $Q_N = 31.8$ G. is 0.153. In view of the approximate nature of HMO calculations and the comparatively arbitrary selection of coulomb and resonance integrals and Q_N , these calculations should be considered as merely indicative.

We do wish to emphasize that the assumption that the TDE⁺ radical is strictly coplanar probably is inadequate. Two reasonable geometric distortions may be considered: (a) twisting about the carbon-carbon bond axis and (b) rotation of the "planar" dimethylamino groups about the nitrogen-ethylene carbon bond. Some estimate of the effect of these distortions on the spin densities in TDE⁺ is possible by variation of appropriate resonance integrals in the HMO calculations.

For distortion (a) the calculated nitrogen spin density decreases from 0.125 to 0.113 when β_{CC} is decreased to $0.7\beta_{CC}$ with $\sigma = 1$. Wiberg and Buchler² have suggested on the basis of infrared data that distortion (a) occurs in TDE⁺. However, since the calculated π -bond order for the carbon-carbon bond in TDE⁺ is 0.56 as compared with only 0.23 for TDE⁺ distortion (a) should be much less important for TDE⁺ than for TDE⁺.

Distortion (b) is effectively the deviation of the nitrogen p_z -orbital from a position strictly perpendicular to the C-C-N plane. Calculations were done by letting $\beta_{CN} = \beta_{CC} \cos^2 \theta$, where θ is the projected angle between the ethylene carbon and nitrogen p_z -orbitals. With $\sigma = 1$ the nitrogen spin density decreases only slightly for $\theta = 30^\circ$ but goes to 0 for $\theta = 90^\circ$. A more rigorous examination of this distortion must incorporate the fact that for extreme twisting (large values of θ) the flat dimethylamino group (sp^3 hybridization) will assume a pyramidal configuration. Cole¹⁷ has commented that if the H_3N^+ radical were pyramidal the nitrogen coupling constant would be considerably larger, a fact that Tench used to support the assignment of a planar structure to $(CH_3)_3N^+$. Just recently Giacometti and Nordio¹⁹ have estimated the nitrogen coupling for a pyramidal H_3N^+ as 66 G. The implication is that the Q_N value in eq. 2 increases for increasing values of θ . However, the concomitant decrease of ρ_N^π for radicals like TDE⁺ is expected to lead to a small value of a_N for extreme examples of distortion (b).

The qualitative description of the relation of nitrogen coupling constants to molecular structure as stated above seems to be applicable to the data of Lemal and Kawano²⁰ for the cation radical I of bis[1,3-diphenylimidazolidinylidene-(2)]. The e.s.r. spectrum in



(19) G. Giacometti and P. L. Nordio, *Mol. Phys.*, **6**, 301 (1963).

(20) D. M. Lemal and K. I. Kawano, *J. Am. Chem. Soc.*, **84**, 1761 (1962).

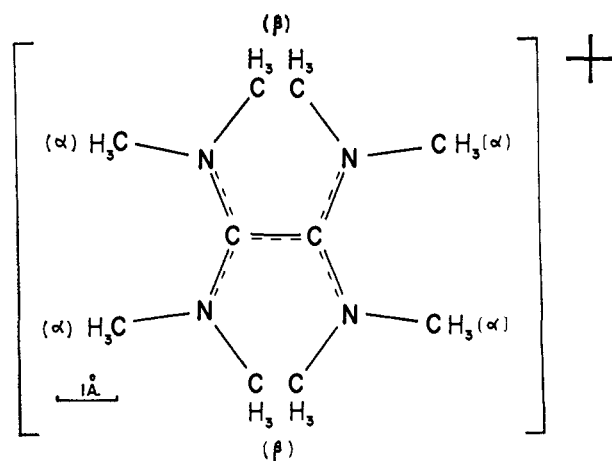


Fig. 3.—Estimated structure of TDE⁺.

chloroform solution consisted of only a single line with a width at maximum slope of 5.4 G. Since such a line could not conceal a very large nitrogen coupling constant for four equivalent nitrogens, the π -electron spin density on the nitrogen atoms apparently is small. Examination of models of I shows that the steric repulsions of the phenyl groups represent a serious barrier to sp^2 hybridization of the nitrogen atom. Thus distortion (b) probably is strongly operative to localize the spin density on the ethylene carbon atoms.^{20a}

The nitrogen coupling constant for TDE⁺ appears to be reasonable for an *approximately* coplanar structure. Derivation of more detailed conformational information from the nitrogen coupling constant must await a more extensive experimental test of the validity of eq. 2²¹ including the dependence of Q_N on θ and more sophisticated spin density calculations.

Methyl Proton Coupling Constants.—We suggest that observation of two different coupling constants, 2.84 and 3.28 G., each for twelve equivalent protons, in TDE⁺ is explicable on the basis of restricted rotation about the ethylene carbon-nitrogen bond. Examination of Fig. 3, an estimate of the structure²² of a hypothetical coplanar TDE⁺, shows that the α - and β -methyl groups have different steric environments. Rapid rotation of the dimethylamino group would average out the different electronic environments at α and β and a single methyl proton coupling constant would be observed. On basis of the line widths of *ca.* 0.05 G. in the experimental e.s.r. spectrum of TDE⁺ the lifetime of the "locked" configuration, as approximated in Fig. 3, which is necessary for observation of

(20a). NOTE ADDED IN PROOF.—When I was obtained by electrooxidation of the parent compound ($E_{1/2} = -0.3$ v. vs. aq. s.c.e.) in dimethylformamide solution the e.s.r. spectrum exhibited a slight resolution of hyperfine structure. The over-all envelope of the spectrum had a width between derivative maxima of 12 G. This result weakens any attempt to set an upper limit on a_N in I.

(21) Karplus and Fraenkel¹⁶ have pointed out that in general there will be some contribution to the total nitrogen coupling constant from adjacent atoms in proportion to the spin density of such atoms. For TDE⁺, such contributions could be significant because of the relatively high spin density on the ethylenic carbon atoms.

(22) The planarity of the related Wurster's blue cation radical, $(CH_3)_2NC_6H_4N(CH_3)_2^+$, has been established by the X-ray crystallographic study of the perchlorate salt by A. C. Albrecht, private communication. The ethylene carbon-nitrogen bond distance of 1.39 Å. in TDE⁺ was taken from Albrecht's work as was the value of 1.47 Å. for the nitrogen-methyl carbon bond, and the methyl carbon-nitrogen-methyl carbon bond angle of 120° . The carbon-carbon bond distance in TDE⁺ was estimated as 1.38 Å. using the semiempirical relation between bond order and bond length as discussed by C. A. Coulson, *Proc. Roy. Soc. (London)*, **A207**, 91 (1951). The carbon-carbon-nitrogen bond angle was taken as 112° , the value for the corresponding bond angle in tetramethylethylene.

two kinds of methyl proton coupling constants is estimated as of the order of microseconds or longer. The absence of any change in the spectrum over a 120° temperature range is evidence for a large energy barrier to rotation about the carbon-nitrogen bond. We suggest that the differing nonbonded interactions between methyl groups and the remainder of the radical are responsible for observation of different spin densities in the α - and β -positions. It should be noted that related phenomena have been observed in the e.s.r. spectra of a number of anion radicals.²³⁻²⁶

Wiberg and Buchler² found that the p.m.r. spectrum of TDE⁺2 showed two absorptions of equal intensity which differed in chemical shift by 0.28 p.p.m. They attributed the observation to the absence of free rotation about the C-N(CH₃)₂ bond and pointed to a similar observation for dimethylformamide.²⁷

The ratio, R , of methyl proton coupling constant to nitrogen coupling constant has values of 0.68 and 0.59

(23) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961).

(24) A. H. Maki, *J. Chem. Phys.*, **35**, 761 (1961).

(25) P. H. Rieger and G. K. Fraenkel, *ibid.*, **37**, 2811 (1962).

(26) E. W. Stone and A. H. Maki, *ibid.*, **38**, 1999 (1963).

(27) W. D. Phillips, *ibid.*, **23**, 1363 (1955).

[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH.]

Keto-Enol Tautomerism in β -Dicarbonyls Studied by Nuclear Magnetic Resonance Spectroscopy.¹ I. Proton Chemical Shifts and Equilibrium Constants of Pure Compounds

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The tautomeric equilibria of β -dicarbonyls have been investigated by nuclear magnetic resonance (n.m.r.) spectroscopy. Proton chemical shift measurements have been made for a series of acyclic compounds, and equilibrium constants ($[\text{enol}]/[\text{keto}]$) have been determined. Substituent effects on proton chemical shifts and on equilibrium constants have been noted.

Keto-enol tautomerism has been studied for many years by techniques such as bromine titration and infrared and ultraviolet spectroscopy. Nuclear magnetic resonance spectroscopy, like other spectroscopic methods, provides the opportunity of investigating the tautomeric equilibrium without affecting the position of the equilibrium itself.

Jarrett, *et al.*,² examined the n.m.r. spectra of acetylacetone and α -methylacetylacetone and showed that the spectra of the tautomers could be distinguished; however, they could not resolve the acetyl methyl or α -methyl protons of the tautomers. Reeves^{3a} studied acetylacetone and Giessner-Prettre^{3b} ethyl acetoacetate by the n.m.r. method. Forsen and Nilsson⁴ have made an extensive investigation of enolized β -triketones using both n.m.r. and infrared spectroscopy.

(1) This work was supported through a contract with the Atomic Energy Commission and a grant from the National Science Foundation, and is abstracted in part from the Ph.D. thesis of Jane L. Burdett, Michigan State University, 1963.

(2) H. S. Jarrett, M. S. Sadler, and J. N. Shooley, *J. Chem. Phys.*, **21**, 2092 (1953).

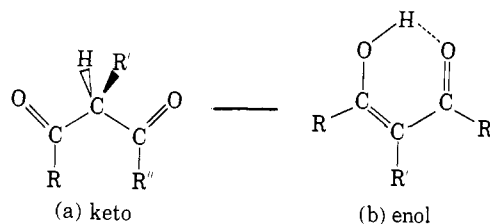
(3) (a) L. W. Reeves, *Can. J. Chem.*, **35**, 1351 (1957); (b) C. Giessner-Prettre, *Compt. rend.*, **250**, 2547 (1960).

(4) S. Forsen and M. Nilsson, *Acta Chem. Scand.*, **13**, 1383 (1959); S. Forsen and M. Nilsson, *ibid.*, **14**, 1333 (1960); S. Forsen and M. Nilsson, *Arkiv Kemi*, **17**, 523 (1961); S. Forsen and M. Nilsson, *ibid.*, **19**, 569 (1962); S. Forsen, M. Nilsson, and C. A. Wachtmeister, *Acta Chem. Scand.*, **16**, 583 (1962); S. Forsen, *Svensk Kem. Tidskr.*, **74**, 439 (1962).

in TDE⁺. These values are anomalously low by comparison with R -values for related radicals such as Wurster's blue, 0.97, and (CH₃)₃N⁺, 1.48. Such low values may arise from enhancement of the nitrogen coupling constant or it is possible that structural perturbations described in the preceding section may be responsible for depression of the methyl proton coupling constant. Whichever the case, there is not now an unequivocal basis for establishing which of the coupling constants should be attributed to the β -methyl protons. We do wish to suggest that the smaller coupling constant of 2.84 G. probably should be identified with the β -methyl protons. This conclusion is based on the naïve argument that the β -methyl protons are subject to a larger nonbonded electronic interaction which in turn is properly correlated with the larger deviation of the R -value of 0.59 from the values of 0.97 and 1.48 as cited above.

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The present study has involved a series of β -dicarbonyls, both β -diketones and β -keto esters, principally of the acyclic variety. The keto-enol tautomeric equilibrium which is considered in this study is shown below where (a) is the keto tautomer and (b) is the enol tautomer. Separate resonance signals are nearly al-



ways observed for the protons of the various groups in the keto and enol tautomers. Identification of these peaks has been possible from the chemical shifts and spin-spin splittings combined with integration of the relative intensities of keto and enol resonances for a given compound. In some cases solvent effects or variable temperature studies have been used to confirm the assignments. For example, dilution in hexane which increases the percentage enol tautomer made it