Quantum mechanical calculations have now progressed to the point where they can set useful lower bounds to binding energy in simple systems. That is, by the variation principle $D_e$ (exp.) $\geq E_{\text{atoms}}$ (exp.) $- E_{\text{molecule}}$(calcd.). We accordingly have carried out an *ab initio* calculation using a $^2\Sigma_u{}^+$ *valence-bond* function with the terms $(1s_a1s_a'1s_b'')$, $(1s_a''2s_a1s_b'')$, $(1s_a2s_a1s_b'')$, $(1s_a1s_a'2s_a)$, $(1s_a1s_a'2p_{oa})$, $(2s_a{}^21s_b'')$, $(2p_{oa}{}^21s_b')$, $(2p_{\pm 1a}1s_b'')$, $(3p^2{}_{oa}1s_b'')$, $(3p_{\pm 1a}1s_b'')$, $(3d_{oa}{}^21s_b'')$, $(3d_{\pm 1a}1s_b'')$, $(3d_{\pm 2a}1s_b'')$ $(1s_a2p_{oa}1s_b'')$, $(1s_a''3p_{oa}''1s_b'')$ $(1s_a''3d_{oa}1s''_b'')$, $(2s_a2p_{oa}1s_b'')$, $(2s_a3p_{oa}1s'')$, $(2p_{oa}3p_{oa}1s_b'')$ $(1s_a''3s_a1s_b'')$, $(3s_a{}^21s_b'')$. Slater orbitals have been used and the primes indicate different orbital exponents on the same orbitals.

The results are listed in Table I together with the results of previous investigations. It is clear that

TABLE I

| Author | $D_e$(e.v.) |
|---|---|
| Pauling,[6] 1st | no binding |
| Pauling, 2nd | 0.05 |
| Weinbaum[7] | 0.7 |
| Moiseiwitsch,[8] 1st | no binding |
| Moiseiwitsch, 2nd | 0.65 |
| Moiseiwitsch, 3rd | 0.76 |
| Csavinszky[9] | 0.84 |
| Present calculation[10] | 2.045 |

we have eliminated the lower bound of 1.4 e.v. obtained by Hornbeck and Molnar[4] and replaced it by the theoretical lower bound[10] of 2.045 e.v. Details of this calculation will be reported in a later publication.

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(6) L. Pauling, *J. Chem. Phys.*, **1**, 56 (1933).

(7) S. Weinbaum, *ibid.*, **3**, 547 (1935).

(8) B. L. Moiseiwitsch, *Proc. Phys. Soc.* (London), **A69**, 653 (1956).

(9) P. Csavinszky, *J. Chem. Phys.*, **31**, 178 (1959).

(10) NOTE ADDED TO PROOF.—With a slightly larger wave function, we have found a new lower bound of 2.14 e.v.

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RECEIVED MAY 11, 1962

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## MOLECULAR STRUCTURE, DIPOLE MOMENT, AND QUADRUPOLE COUPLING CONSTANTS OF DIAZIRINE

*Sir:*

It is now a well established fact that diazomethane and aliphatic diazo compounds do not have the cyclic three-membered ring structure that originally was proposed by early workers in the field of nitrogen chemistry. Recently this same three-membered ring structure has been assigned to a newly discovered class of compounds, diazirine and substituted diazirines.[1,2,3] We have measured the rotational spectrum of diazirine and wish to report that analysis of our data decisively proves the cyclic assignment to be correct.

The sample used in this work was kindly provided by Dr. W. H. Graham.[4] Measurements were made in the frequency region 7.8 to 41 kMc. with a Stark-modulation type microwave spectrometer which has been described previously.[5] Using the Stark effect as a guide, twelve very strong absorptions were assigned as "A" type transitions of the common isotopic species of diazirine in its ground vibrational state. The Stark effect also provided the basis for assignment of eight weaker absorptions to rotational transitions of $H_2{}^{13}CN_2$ (1.1% in natural abundance) and $H_2C^{14}N^{15}N$ (0.7% in natural abundance). Table I lists transition frequencies from which the moments of inertia of Table II were derived by a rigid-rotor analysis.

TABLE I

MICROWAVE SPECTRUM OF DIAZIRINE[a]

| Transition | Frequency, Mc. $H_2CN_2$ | $H_2C^{15}N^{14}N$ | $H_2{}^{13}CN_2$ |
|---|---|---|---|
| $1_{01} \leftarrow 0_{00}$ | 40,394.02 | 39,823.36 | 39,192.40 |
| $2_{11} \leftarrow 2_{12}$ | 20,824.34 | 21,028.55 | 19,639.87 |
| $3_{21} \leftarrow 3_{22}$ | 7,944.33 | 8,380.85 | [b] |
| $4_{22} \leftarrow 4_{23}$ | 20,992.62 | 21,947.91 | 18,648.46 |

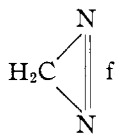
[a] The frequencies reported for $H_2C^{15}N^{15}N$ are "zeroth-order" frequencies, *i.e.*, observed frequencies corrected for quadrupole coupling effects. Transition frequencies given for the other species are averages over partially resolved fine structure components. [b] Not observed.

TABLE II

GROUND-STATE ROTATIONAL CONSTANTS (Mc) AND MOMENTS OF INERTIA (amu.-A.$^2$) OF DIAZIRINE[a]

| | $H_2CN_2$ | $H_2C^{15}N^{14}N$ | $H_2{}^{13}CN_2$ |
|---|---|---|---|
| A | 40,956.72 | 39,802.62 | 40,954.83 |
| B | 23,667.76 | 23,416.43 | 22,869.51 |
| C | 16,726.26 | 16,406.93 | 16,322.89 |
| $I_A$ | 12.34305 | 12.70095 | 12.34362 |
| $I_B$ | 21.35948 | 21.58873 | 22.10502 |
| $I_C$ | 30.22379 | 30.81204 | 30.97068 |

[a] Conversion factor: $h/8\pi^2$ = 505,531 Mc.-amu.-A.$^2$.

Assumption of the cyclic structure  for diazirine requires that the carbon atom lie on a $C_2$ axis of symmetry. The fact that "A" type rotational transitions are observed for diazirine further requires that this $C_2$ axis be the axis of least inertia (the A-axis). An important consequence of the above is that when $^{13}C$ is substituted for $^{12}C$, the changes $\Delta I$ in the principal moments of inertia must satisfy (in the rigid rotor approximation) the equations

$$\Delta I_A = 0 \qquad \Delta I_B = \Delta I_C \qquad (1)$$

From the assignments of Table I, we find $\Delta I_A$ = 0.0006 and $\Delta I_B$ = 0.7456 and $\Delta I_C$ = 0.7469 amu.-Å.$^2$. A further requirement of the above assumption is that $d_{NN}$, the N–N bond distance, be given (again in the rigid rotor approximation) by

$$d_{NN} = [m_N{}^{-1}(I_a + I_c - I_b)]^{1/2} \qquad (2)$$

where $m_N$ is the mass of the nitrogen atom and the $I$'s refer to principal moments of inertia of any symmetrical isotopic species of diazirine. From our assignments for $H_2CN_2$ and $H_2{}^{13}CN_2$ we obtain the respective values 1.2304 Å. and 1.2305 Å. for $d_{NN}$. An independent determination of $d_{NN}$ which makes

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(1) S. R. Paulsen, *Angew. Chem.*, **72**, 781 (1960).

(2) E. Schmitz and R. Ohme, *Tetrahedron Letters*, 612 (1961).

(3) W. H. Graham, *J. Am. Chem. Soc.*, **84**, 1063 (1962).

(4) The methods by which the sample was prepared and identified as diazirine are given by W. H. Graham in the previous reference.

(5) J. M. O'Reilly and L. Pierce, *J. Chem. Phys.*, **34**, 1176 (1961).

use of the *changes* in moments of inertia(6) with substitution of $^{15}N$ for $^{14}N$ gives $d_{NN} = 1.228$ Å. The assignments of Table I are thus strikingly consistent with the assumption of a cyclic structure for diazirine. Interatomic distances and angles as derived from the data in Table II are given in Table III.

TABLE III

MOLECULAR PARAMETERS OF DIAZIRINE[a]

$d_{NN} = 1.228 \pm 0.003$ Å. $d_{CH} = 1.09 \pm 0.02$ Å.
$d_{CN} = 1.482 \pm 0.003$ Å. $\angle HCH = 117° \pm 2°$
$\chi_{CC} - \chi_{BB} = 6.2 \pm 0.3$ Mc. $|\chi_{AA}| < 1.0$ Mc.
$\mu = 1.59 \pm 0.06$ Debye

[a] The structural parameters $d_{CN}$ and $d_{NN}$ are so-called $r_s$ parameters[7] since they were obtained by using only *isotopic shifts* in the *moments* of *inertia*.

The small quadrupole moment of the nitrogen ($^{14}N$) nucleus makes difficult the task of resolving hyperfine structure in the rotational spectrum of $H_2CN_2$ and $H_2{}^{13}CN_2$. The problem is much simpler for $H_2C^{14}N^{15}N$ which contains only one quadrupolar nucleus. From the observed Q-branch splittings for this species, we find $\chi_{CC} - \chi_{BB} = 6.2 \pm 0.3$ Mc. The $1_{01} \leftarrow 0_{00}$ transition depends only on the quadrupole coupling parameter $\chi_{AA}$. We found it impossible to resolve any hyperfine structure in the $1_{01} \leftarrow 0_{00}$ transition for any of the three isotopic species. From observed line widths (0.5 Mc.) we conclude that $|\chi_{AA}| < 1$ Mc.

From Stark effect measurements on the $M = 4$ and $M = 3$ Stark components of the $4_{22} \leftarrow 4_{23}$ transitions of the common isotopic species of diazirine, we find the dipole moment to be $1.59 \pm 0.06$ *D*. The rather large error assigned to the dipole moment is a result of the fact that quadrupole coupling effects make difficult the measurement of Stark shifts.

**Acknowledgments.**—We are very grateful to Dr. W. H. Graham for providing the sample of diazirine used in this work, and to Bro. C. R. Nelson and Fr. Cyprian Flanagan for their valuable assistance in certain aspects of the experimental work. Support for this research was provided by the National Science Foundation.

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(6) The rotational isotope effect is fully discussed for asymmetric rotor molecules in the rigid rotor approximation by J. Kraitchman, *Am. J. Phys.*, **21**, 17 (1953).

(7) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).

(8) Alfred P. Sloan Foundation Fellow.

(9) Recipient, DuPont Teaching Assistant Award 1961–1962.

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## AUTOXIDATION AND CONDENSATION REACTIONS OF CARBANIONS IN DIMETHYL SULFOXIDE SOLUTION(1)

*Sir:*

A recent communication by Corey and Chaykovsky,(2) concerning the methylsulfinyl carbanion and its reactions, prompts us to report some results concerning the autoxidation of carbanions in dimethyl sulfoxide solution—a study which has led to an investigation of condensation and addition reactions involving dimethyl sulfoxide. Although solutions of alkoxides in dimethyl sulfoxide react with oxygen yielding dimethyl sulfone and methanesulfonic acid, mixtures of dimethyl sulfoxide and *t*-butyl alcohol are stable to oxygen at room temperature in the presence of potassium *t*-butoxide. In these solutions (DMSO–*t*-BuOH–*t*-BuO$^-$) a number of hydrocarbons can be oxidized easily. In many cases similar oxidations in alcohol or pyridine solutions are not observed.

TABLE I

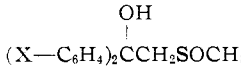
AUTOXIDATION OF DIARYLMETHANES IN DMSO–*t*-BuOH–*t*-BuO$^-$ SOLUTION AT 25°

| Diarylmethane, mmole | *t*-BuOK, mmole | Time, min. | mmole $O_2$ | Product, mmole |
|---|---|---|---|---|
| Diphenylmethane, 3.0 | 6.3[a] | 10 | 5.1 | Benzhydrol, 1.8 |
| Diphenylmethane, 3.0 | 15[a] | 120 | 9.6 | I, X = H, 1.9 |
| Fluorene, 3.2 | 6.0[b] | 0.5 | 3.0 | I,[c] 2.4 |
| Xanthene, 3.1 | 6.0[b] | 2.5 | 4.2 | Xanthone, 3.1 |
| 9,10-Dihydroanthracene, 3.2 | 9.0[d] | 5 | 6.5 | Anthracene, 2.35 |

[a] 35 ml. of 80–20 DMSO–*t*-BuOH. [b] 25 ml. of solvent. [c] M.p. 155.5–156.5°. [d] 50 ml. of solvent.

Triphenylmethane reacts with oxygen under these conditions to form triphenylcarbinol. Triphenylmethane (3.14 mmole) in 25 ml. of vigorously shaken 80–20 DMSO–*t*-BuOH solution containing 6 mmole of potassium *t*-butoxide absorbed 3.2 mmole of oxygen (740 mm.) in 20 minutes (2.6 mmole in two minutes) to yield 3.0 mmole of triphenylcarbinol. In the absence of oxygen, triphenylmethane-*d* lost 53% of its deuterium in five minutes at 25° even though the color of the triphenylmethide ion could not be detected as it can be in the absence of the *t*-butyl alcohol.

Diarylmethanes are oxidized readily under similar conditions to either the alcohol, the ketone or the dimethyl sulfoxide adduct of the ketone (I).



$$(X{-}C_6H_4)_2\overset{\displaystyle OH}{\overset{|}{C}}CH_2SOCH_3$$

I

The oxidation of fluorene in *t*-butyl alcohol–*t*-butoxide solution is strongly catalyzed by nitrobenzene or 1,3-dinitrobenzene (3 mole %). In the absence of oxygen the nitrobenzene radical anion(3) can be detected by e.s.r. These results strongly support the concept that the oxidation of fluorene and the other arylmethanes is a radical process.(4)

Substituted toluenes ($CH_3{-}C_6H_4{-}X$, X = $SO_2C_6H_5$, $CO_2CH_3$, $COC_6H_5$, $COOCH_3$, CN, $N{=}NC_6H_5$, $SOC_6H_5$, $NO_2$) and a variety of *o*-, *m*- and *p*-substituted anilines readily undergo base-promoted autoxidation in dimethyl sulfoxide solution at room temperature whereas, with the exception of *p*-nitrotoluene, these compounds are stable to oxygen in *t*-butyl alcohol–*t*-butoxide solutions. The oxidations of phenyl *p*-tolyl sulfone and methyl *p*-toluate have been studied in more detail and are considered as representative of the other substituted toluenes except for *p*-nitrotoluene.(5)

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(1) Reactions of Resonance Stabilized Anions. II.

(2) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

(3) D. H. Geske and A. H. Maki, *ibid.*, **82**, 2671 (1960); R. L. Ward, *ibid.*, **83**, 1296 (1961).

(4) See, however, Y. Sprinzak, *ibid.*, **80**, 5449 (1958).

(5) See G. A. Russell, Abstracts of Papers, 17th National Organic Chemistry Symposium, Bloomington, Ind., 1961, p. 71.