with silver oxide yielded dibasic acid IV (m.p. 181–183°. *Anal.* Calcd.: neutr. equiv., 78. Found: 79) with similar n.m.r. spectrum (D_3CCOCD_3, TMS) save for a downfield singlet at τ −0.3 accounting for the two carboxyl protons and for the missing aldehyde proton signal. The melting point of IV failed to agree with that of any of the reported[10] dicarboxylic acids of cyclopentene. Rigorous structure proof is being undertaken in view of possible further carbon skeleton rearrangements.

Acknowledgment. We are indebted to Professor Paul Bartlett for suggesting this tropolone synthesis and for discussions during its course.

(10) A. Hassel and C. K. Ingold, *J. Chem. Soc.*, 1465 (1926); B. L. Nandi, *J. Indian Chem. Soc.*, 11, 277 (1934); S. Fujise, H. Uda, T. Ishikawa, H. Obaia, and A. Fujino, *Nippon Kagaku Zasshi*, 81, 1871 (1960); P. C. Guha and D. K. Sankaran, *Ber.*, 70, 2109 (1937).

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The Microwave Spectrum of Dinitrogen Trioxide

Sir:

Pure dinitrogen trioxide cannot be isolated in the gas phase since it exists in equilibrium with its dissociation products NO and NO_2.[1] Infrared[2] and chemical evidence[3] have supported the planar structure with a long N–N bond
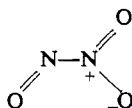
At low temperature and pressures, we have observed the microwave spectrum of four isotopic species of N_2O_3 which support the planar model and from which the N–N bond is determined to be 1.85 ± 0.03 Å.

The spectra were produced at about 0.1 mm. by mixing NO and NO_2–N_2O_4 at about equal pressure in an absorption cell cooled to −78°. The spectra could not be observed at room temperature. Equilibrium calculations[1,4] gave pressures for N_2O_3 of about 1×10^{-3} mm. at −78° and about 1×10^{-6} mm. at room temperature, which correlate with this observed temperature dependence of the intensity. The ratio of observed intensity (roughly 10^{-7}–10^{-8} cm.$^{-1}$) to calculated intensity (10^{-5} cm.$^{-1}$) indicated that the N_2O_3 was about 0.1–1% of the total mixture, which also agrees with equilibrium calculations.

When $^{14}NO_2$ was mixed with 97%-enriched ^{15}NO, absorption lines from three additional species were observed in relative intensity approximately equal to the normal isotopic species. Since the reaction $^{15}NO + {}^{14}NO_2 \rightleftarrows {}^{14}NO + {}^{15}NO_2$ is known,[5] the presence of four isotopic species shows that the absorbing species contains two nonequivalent nitrogen atoms.

Several of the observed transitions, assigned by the Stark effect and frequency fit, are listed in Table I.

(1) I. R. Beattie, *Progr. Inorg. Chem.*, 5, 1 (1960).
(2) J. P. Devlin and I. C. Hisatsune, *Spectrochim. Acta*, 17, 218 (1961).
(3) C. K. Ingold and E. H. Ingold, *Nature*, 159, 743 (1947).
(4) I. C. Hisatsune, *J. Phys. Chem.*, 65, 2249 (1961).
(5) E. Leifer, *J. Chem. Phys.*, 8, 301 (1940).

Table I. Microwave Spectrum of N_2O_3 (Mc./sec.)ᵃ

Transition	Observed	Calculated
$O^{14}N^{14}NO_2$		
$2_{02} \rightarrow 3_{03}$	21750.30	21750.30
$2_{12} \rightarrow 3_{13}$	20469.14	20469.17
$2_{11} \rightarrow 3_{12}$	23684.06	23684.10
$2_{21} \rightarrow 3_{22}$	22138.32	22138.35
$2_{20} \rightarrow 3_{21}$	22525.94	22526.40
$O^{15}N^{14}NO_2$		
$2_{02} \rightarrow 3_{03}$	21532.19	21532.16
$2_{12} \rightarrow 3_{13}$	20262.25	20262.25
$2_{11} \rightarrow 3_{12}$	23454.32	23454.31
$3_{03} \rightarrow 4_{04}$	28289.72	28290.06
$3_{12} \rightarrow 4_{13}$	31143.56	31143.82
$O^{14}N^{15}NO_2$		
$2_{02} \rightarrow 3_{03}$	21692.38	21692.34
$2_{12} \rightarrow 3_{13}$	20416.07	20416.06
$2_{11} \rightarrow 3_{12}$	23613.07	23613.04
$3_{03} \rightarrow 4_{04}$	28507.34	28507.89
$3_{12} \rightarrow 4_{13}$	31356.87	31357.26
$O^{15}N^{15}NO_2$		
$2_{02} \rightarrow 3_{03}$	21472.78	21472.77
$2_{12} \rightarrow 3_{13}$	20208.04	20208.08
$2_{11} \rightarrow 3_{12}$	23381.64	23381.65
$3_{03} \rightarrow 4_{04}$	28215.30	28215.69
$3_{12} \rightarrow 4_{13}$	31048.14	31048.65

ᵃ Obtained with a conventional Stark modulated spectrometer. Frequencies are reproducible to ± 0.2–0.3 Mc./sec.

Table II. Rotational Constants (Mc./sec.) and Moments of Inertia (a.m.u. Å²) for N_2O_3ᵃ

	$O^{14}N^{14}NO_2$	$O^{15}N^{14}NO_2$	$O^{14}N^{15}NO_2$	$O^{15}N^{15}NO_2$
A	12,453	12,296	12,458	12,295
B	4,226.49	4,186.29	4,213.00	4,172.49
C	3,152.96	3,120.37	3,145.49	3,112.77
I_a	40.60	41.11	40.58	41.12
I_b	119.6101	120.7587	119.9931	121.1581
I_c	160.3354	162.0100	160.7161	162.4055
Δ	0.13	0.14	0.14	0.13

ᵃ The experimental uncertainties in A and $B = C$ are ±6 and ±0.05 Mc./sec., respectively; conversion factor, 5.05531×10^5 a.m.u. Å.² Mc./sec.

Quadrupole splitting due to the ^{14}N nucleus was not resolved. The moments of inertia are listed in Table II.

The observed value of $\Delta = I_c - I_b - I_a$ (inertial defect) is typical of planar molecules. Any appreciable deviation from planarity should give a negative value easily detectable owing to the large masses of the atoms. However, slight deviations from planarity cannot be eliminated on this basis alone. It is reasonable to conclude, therefore, that the moments of inertia support a planar or very nearly planar species.

The N–N bond length can be determined from the moments of inertia of three isotopic species.[6] Using the sets $O^{14}N^{14}NO_2$, $O^{14}N^{15}NO_2$, $O^{15}N^{14}NO_2$, and $O^{15}N^{15}NO_2$, $O^{15}N^{14}NO_2$, $O^{14}N^{15}NO_2$, almost identical values of 1.850 and 1.853 Å. were obtained. Therefore, the N–N bond length is evaluated at 1.85 ± 0.03 Å. The large uncertainty is considered sufficient to include errors introduced because the "nitro" nitrogen lies close to the "a" axis and because $I_c - I_b$ was substituted for the more uncertain I_a in Kraitchman's equations.[7] For comparison, the N–N bond in N_2H_4

(6) J. Kraitchman, *Am. J. Phys.*, 21, 17 (1953).
(7) V. W. Laurie, D. T. Pence, and R. H. Jackson, *J. Chem. Phys.*, 37, 2995 (1962).

is 1.45 Å.,[8] and in N_2O_4 it is 1.75 Å.[9] Therefore in N_2O_3 this distance is unusually long although it is still considerably shorter than twice the van der Waal's radius for nitrogen of 3 Å.[10] The infrared analysis has also favored a long bond.[2]

A complete structure determination independent of any assumptions is not possible without data from another isotopic species. From calculations it is clear, however, that the observed data will fit a range of planar $ON-NO_2$ models with C_s symmetry and $d(NN)$ = 1.85 Å., and with N–O bond lengths and interatomic angles similar to those observed in other molecules.[11,12] This is the model for N_2O_3 which has been generally accepted and supported in the literature.[1,2]

In summary, the basis for asserting that the observed spectra arises from N_2O_3 is as follows. (1) The reaction of NO and NO_2 produces the spectra which have intensity and pressure–temperature dependence of the intensity in agreement with equilibrium calculations. (2) The spectrum arises from a species containing two nonequivalent nitrogen atoms separated by 1.85 ± 0.03 Å. (3) The moments of inertia will fit a planar $ON-NO_2$ model with C_s symmetry, a long N–N bonded distance and with N–O bond lengths and angles similar to other compounds.

Acknowledgment. The author thanks Dr. David R. Lide, Jr., and Dr. William H. Kirchhoff for numerous helpful discussions concerning this work.

(8) A. Yamaguchi, I. Ichishima, T. Shimanouchi, and S. Mizushima, *Spectrochim. Acta*, 16, 1471 (1960).
(9) D. W. Smith and K. Hedberg, *J. Chem. Phys.*, 25, 1282 (1956).
(10) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1948, p. 189.
(11) A. P. Cox and J. M. Riveros, *J. Chem. Phys.*, 42, 3106 (1965).
(12) D. W. Magnuson, *ibid.*, 19, 1071 (1952).
(13) National Research Council–National Bureau of Standards Postdoctoral Associate.

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Electron Spin Resonance Studies of Deuterium Isotope Effects. A Novel Resonance-Integral Perturbation[1]

Sir:

Recent electron spin resonance (e.s.r.) studies of aromatic radicals have demonstrated that the replacement of a hydrogen atom by deuterium can produce significant modifications in the proton hyperfine splitting constants (a^H) for ring positions other than the one of substitution. The most dramatic effect is observed in the benzene anion[2]; smaller changes occur in the deuterated naphthalene anions[3] and in the N-deuterated dihydropyrazine cation and its methyl derivatives.[4] In striking contrast to the result for benzene, deuteration does not alter the proton hyperfine splittings in the cyclooctatetraene anion radical.[5] In this communication, we propose that a consistent explanation of these

(1) Research supported in part through U. S. Air Force Office of Scientific Research Grants No. AF-AFOSR-285-63 and -65.
(2) R. G. Lawler, J. R. Bolton, G. K. Fraenkel, and T. H. Brown, *J. Am. Chem. Soc.*, 86, 520 (1964).
(3) R. G. Lawler, J. R. Bolton, G. K. Fraenkel, and M. Karplus, to be published.
(4) M. R. Das and G. K. Fraenkel, *J. Chem. Phys.*, 42, 792 (1965).
(5) A. Carrington, H. C. Longuet-Higgins, R. E. Moss, and P. F. Todd, *Mol. Phys.*, 9, 187 (1965).

data is provided by a vibrational perturbation of the Hückel resonance-integral parameter β. The nature of the effect, which is different from the electron donation usually associated with deuteration,[6] is such that it should occur in general on isotopic substitution of aromatic hydrocarbons.

To provide a qualitative description of the alteration of the electronic wave function on deuteration, we consider a very simple model. If the carbon-atom $2p\pi$ orbitals follow the out-of-plane bending motion of the C–H or C–D bonds, the integral β depends on the hydrogen or deuterium position. For adjacent carbon atoms r and s, we express the effective resonance integral as $\beta_{rs} \cong \beta_0\langle\cos\theta\rangle_{rs}$, where β_0 is the resonance-integral parameter corresponding to a pair of parallel $2p\pi$ orbitals, θ is a function of the angle between them, and $\langle\rangle$ signifies a vibrational average. Expanding $\cos\theta$, we obtain $\delta_{rs} = \beta_{rs}{}^D - \beta_{rs}{}^H \cong (\beta_0/2)[\langle\theta^2\rangle_{rs}{}^H - \langle\theta^2\rangle_{rs}{}^D]$ for the change in β_{rs} on the substitution of deuterium at carbon atom r (or s). Although quantitative evaluation of β_{rs} requires an exact knowledge of the degree of orbital following[7] and a complete vibrational analysis for the deuterated and undeuterated species, it is evident that $\langle\theta^2\rangle_{rs}{}^H > \langle\theta^2\rangle_{rs}{}^D$, and therefore that $\delta_{rs} < 0$. The energy shift of the Hückel molecular orbital ψ_k for a species deuterated at position r is then[8]

$$\Delta\epsilon_k \cong 2\delta_{r,r+1}c_r{}^{(k)}c_{r+1}{}^{(k)} + 2\delta_{r,r-1}c_r{}^{(k)}c_{r-1}{}^{(k)} \quad (1)$$

where $c_r{}^{(k)}$ is the coefficient of the $2p\pi$ orbital on atom r in ψ_k.

To apply eq. 1 to the benzene-1-d anion we must consider the degenerate pair of antibonding orbitals that are available for the unpaired electron. The orbital which is antisymmetric with respect to the symmetry plane through position 1 is unaltered by the perturbation ($c_1 = 0$), while the symmetric orbital is *destabilized* by $-(^2/_3)\delta$, where $\delta = \delta_{1,2} = \delta_{1,6}$. Thus, in agreement with experiment, the degeneracy is lifted by deuteration and the unpaired electron is predicted to be predominantly in the antisymmetric orbital. A considerable contribution from the symmetric orbital is also expected, however, because of thermal excitation[9] and vibronic coupling.[10] A crude estimate[11] for $C_6H_5D^-$ gives $(\delta/\beta_0) \cong 0.0025$, and on the basis of thermal mixing (with $\beta_0 \cong -40$ kcal./mole) yields the hyperfine constants $a_{para}{}^H = -3.4$ gauss, $a_{ortho}{}^H \cong a_{meta}{}^H = -3.9$ gauss, in agreement with the measured values.[2,12] For the cyclooctatetraene-1-d anion, application of eq. 1 does not remove the degeneracy because a pair of nonbonding orbitals is involved; the model thus predicts no change in the proton hyperfine splittings on deuteration, which is again in agreement with the observed results.[13] The naphthalene negative

(6) E. A. Halevi, *Progr. Phys. Org. Chem.*, 1, 109 (1963).
(7) D. M. Schrader and M. Karplus, *J. Chem. Phys.*, 40, 5093 (1964).
(8) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London), A191, 39 (1947).
(9) T. H. Brown and M. Karplus, *J. Chem. Phys.*, 39, 1115 (1963).
(10) A. D. McLachlan and H. M. McConnell, *ibid.*, 34, 1 (1961).
(11) This value was obtained by assuming complete orbital following and averaging approximately over the out-of-plane vibrations for benzene-1-d at −100°.
(12) R. G. Lawler and G. K. Fraenkel, to be published.
(13) An alternative model given by Carrington, *et al.*,[5] also explains the qualitative differences between the behavior of $C_6H_5D^-$ and $C_8H_7D^-$, but a rough quantitative estimate based on force-constant data [H. P. Fritz, *Advan. Organometal. Chem.*, 1, 239 (1964)] suggests that the effect is too small to account for the hyperfine constant change in $C_6H_5D^-$.