

technique would yield an improved correlation. In particular, we wish to point out that this type of correlation indeed accounts for the peculiar variation in  $^{13}\text{C}$ -F coupling constants<sup>7</sup> for the series  $\text{CFH}_3$  (157.4 c.p.s.),  $\text{CF}_2\text{H}_2$  (234.8 c.p.s.),  $\text{CF}_3\text{H}$  (274.3 c.p.s.), and  $\text{CF}_4$  (259.2 c.p.s.).

This empirical correlation should be useful in the development of theories concerning nuclear magnetic dipole interactions and molecular wave functions. At the present time we are investigating these theoretical aspects. Also, we are investigating other systems in the light of this correlation.

**Acknowledgment.**—The authors gratefully acknowledge the support of the U. S. Army Research Office (Durham), Contract No. DA-31-124-ARO(D)-90.

(10) National Defense Fellow, Department of Health, Education, and Welfare.

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING  
STEVENS INSTITUTE OF TECHNOLOGY  
HOBOKEN, NEW JERSEY

EDMUND R. MALINOWSKI  
THEODORE VLADIMIROFF<sup>10</sup>

RECEIVED MAY 28, 1964

### Ring Inversion and Bond Shift in Cyclooctatetraene Derivatives

Sir:

In order to obtain further information on the ring inversion<sup>1</sup> and bond shift processes<sup>2</sup> in cyclooctatetraene and its derivatives, we have examined the proton n.m.r. spectra,<sup>3</sup> with double irradiation at the deuteron frequency, of ethyl cyclooctatetraene-2,3,4,5,6,7-*d*<sub>6</sub>-carboxylate (I) and of cyclooctatetraenyl-2,3,4,5,6,7-*d*<sub>6</sub>-dimethylcarbinol (II). Compound I was prepared by photochemical addition<sup>4</sup> of ethyl propionate to benzene-*d*<sub>6</sub>. Compound II was obtained by the reaction<sup>5</sup> of I with excess methylmagnesium iodide. These compounds were chosen because they were expected to give particularly simple spectra.<sup>6</sup>

At low temperatures ( $-35^\circ$ ) the ring proton of II ( $\text{CS}_2$  solution) gave rise to two sharp lines of equal intensities separated by 2.6 c.p.s. The high-field band ( $\tau$  4.24) is assigned to the proton in IIa and IIb and the low-field band ( $\tau$  4.20) to the proton in IIc and IID because only the high-field band remained sharp in the absence of deuterium decoupling. The proton in IIa or IIb should<sup>2</sup> show a negligible coupling to the adjacent deuteron whereas the proton in IIc or IID should<sup>2</sup> show an appreciable coupling. The methyl protons also gave two bands ( $\tau$  1.16 and  $\tau$  1.21, separation = 3.3 c.p.s.), as expected<sup>7</sup> from a structure such

(1) The ring inversion process has only been studied quantitatively in dibenzocyclooctatetraenedicarboxylic acid that is rather distantly related to the structure of cyclooctatetraene itself. The activation energy for inversion was found to be 27 kcal./mole [K. Mislow and H. D. Perlmutter, *J. Am. Chem. Soc.*, **84**, 3591 (1962)]. See also N. L. Allinger, W. Szkrybals, and M. A. DaRooge, *J. Org. Chem.*, **28**, 3007 (1963).

(2) F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 671 (1962); G. M. Whitesides and J. D. Roberts, D. E. Gwynn and J. D. Roberts, unpublished observations, quoted by J. D. Roberts, *Angew. Chem.*, **75**, 20 (1963).

(3) Spectra were measured on a Modified Varian HR60 at 60 Mc./sec. The modification consisted of a field-frequency control of the type used by R. Freeman and D. H. Whiffen, *Proc. Phys. Soc. (London)*, **79**, 794 (1962). An NMR Specialties Model SD60 decoupler was used to provide the second radiofrequency (ca. 9.1 Mc. sec.) for double irradiation.

(4) D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, 695 (1963); E. Grovenstein and D. V. Rao, *Tetrahedron Letters*, No. 4, 148 (1961).

(5) A. C. Cope and R. M. Pike, *J. Am. Chem. Soc.*, **75**, 3320 (1953).

(6) F. A. L. Anet and J. S. Hartman, *ibid.*, **85**, 1204 (1963).

(7) P. M. Nair and J. D. Roberts, *ibid.*, **79**, 4565 (1957).

as IIa, in which the two methyl groups are chemically nonequivalent. These two bands are not very sharp and it appears that the methyl groups are slightly coupled to one another.

As the temperature was increased the methyl doublet broadened, then coalesced (at  $-2^\circ$ ), and finally became a single sharp line. The doublet arising from the ring proton showed a similar behavior except that the coalescence temperature was much higher ( $+41^\circ$ ). Since the separation of the ring proton doublet is actually slightly smaller than that of the methyl doublet, the specific rate<sup>8</sup> at which the ring proton changes its environment (*e.g.*, IIa to IIb) must be very much smaller at the same temperature than the specific rate at which the methyl groups exchange their environments.

The processes which average the environments of the two methyl groups are IIa  $\rightarrow$  IIb and IIa  $\rightarrow$  IID. On the other hand, the processes IIa  $\rightarrow$  IIc and IIa  $\rightarrow$  IID contribute to the averaging of the environments of the ring proton. Although the rates of these two latter processes could be different, they must be the same if the transition state for the bond shift is planar, as will be assumed in the following discussion. From the n.m.r. results mentioned above, it can be seen that  $k_1 + k_2/2 \gg k_2$ , so that  $k_1 \gg k_2$ , and therefore the rate constant obtained from the methyl protons is effectively  $k_1$ , the rate constant for ring inversion (without bond shift).

The enthalpy and entropy of activation for bond shift (Table I) were obtained<sup>6,8</sup> by measurements of the rate constant from 26 to  $66^\circ$ . Because of the broadened nature of the methyl bands below the coalescence temperature, corresponding parameters of meaningful accuracy for ring inversion have not yet been obtained.

TABLE I  
KINETIC PARAMETERS FOR BOND SHIFT AND RING  
INVERSION IN CYCLOOCTATETRAENE DERIVATIVES

| Compound | Temp.,<br>°C | Process        | $k$<br>(sec. <sup>-1</sup> ) | $\Delta F^*$<br>(kcal./mole) | $\Delta H^*$ | $\Delta S^*$<br>(e.u.) |
|----------|--------------|----------------|------------------------------|------------------------------|--------------|------------------------|
| I        | 40           | Bond shift     | 126                          | 15.3                         | 12.8         | -8.0                   |
| II       | 41           | Bond shift     | 5.4                          | 17.4                         | 15.4         | -6.3                   |
| II       | -2           | Bond shift     | 0.1 <sup>a</sup>             | 17.1 <sup>a</sup>            |              |                        |
| II       | -2           | Ring inversion | 7.8                          | 14.7                         |              |                        |

<sup>a</sup> Extrapolated.

Evidence for a planar (or nearly planar) transition state for bond shift comes from a comparison of the specific rates of bond shift in II (0.04 sec.<sup>-1</sup>, extrapolated) and in cyclooctatetraene<sup>2</sup> itself (26 sec.<sup>-1</sup>) at the same temperature ( $-10^\circ$ ). The lower specific rate of bond shift in II can be ascribed to greater repulsive interactions of the  $\text{C}(\text{CH}_3)\text{OH}$  group with the adjacent CH and CD groups in the transition state than in the ground state. If the transition state were highly puckered, the reverse order would be expected. This, of course, does not rule out a slight amount of puckering in B. The specific rate of bond shift (2.6 sec.<sup>-1</sup>, extrapolated) in I (see below) at  $-10^\circ$  is intermediate between the two values above as expected

(8) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956); J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, N. Y., 1959, p. 218.

from the relative sizes of the H, COOEt, and C(CH<sub>3</sub>)<sub>2</sub>-OH groups. The negative entropy of activation (Table I) is also in agreement with a planar transition state for bond shift.

The transition state for ring inversion is most likely the planar form A (Fig. 1) that has alternate single and double bonds; on the other hand, the planar transition state B for bond shift has equal bond lengths. From the rate data, it follows that the free-energy difference at -2° between A and B amounts to 2.4 kcal./mole, with A the more stable form.

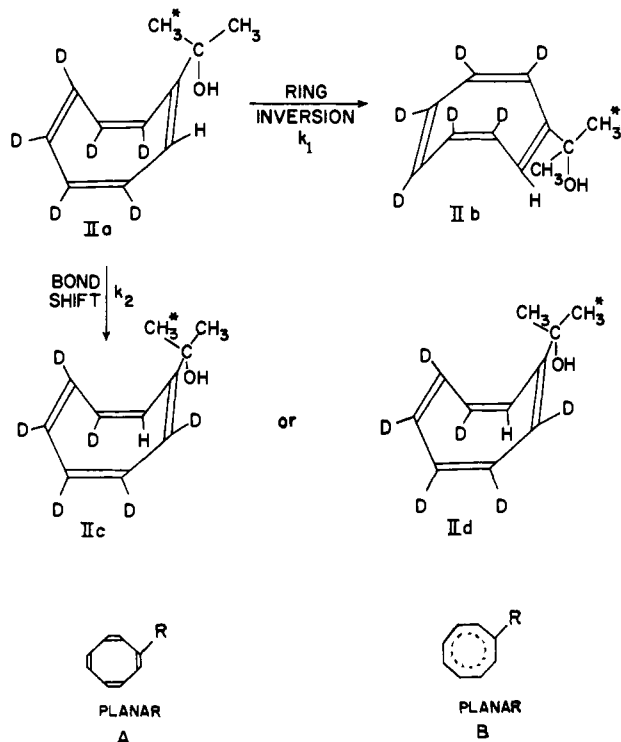


Figure 1.

Structure B has an orbitally degenerate  $\pi$ -electron system and, according to the Jahn-Teller theorem,<sup>9</sup> a distortion of the molecule to make the carbon-carbon bonds alternately shorter and longer will result in stabilization. This stabilization energy can therefore be equated with the energy difference between A and B. Theoretical calculations of the difference in (potential) energy between A and B are rather discordant, although they all show that A should be the more stable state. The values are 44,<sup>10</sup> 0.02,<sup>11</sup> and 1.3<sup>12</sup> kcal./mole. The last of these is in good agreement with the value obtained from the n.m.r. measurements.

The n.m.r. spectrum of I in carbon tetrachloride solution at -30° showed bands of equal intensities at  $\tau$  3.09 and 4.11 which are assigned to the ring protons in IIa and IIc (C(CH<sub>3</sub>)<sub>2</sub>OH replaced by COOEt in both cases), respectively. The two bands broadened at higher temperatures and coalesced at +40°. The rate constant for bond shift was obtained over the temperature range -15 to +75°. Values of  $\Delta H^*$  and  $\Delta S^*$  are given in Table I.

Further work on the n.m.r. spectra of cyclooctatetraene derivatives is in progress.

- (9) H. A. Jahn and E. Teller, *Proc. Roy. Soc. (London)*, **A161**, 220 (1937).  
 (10) N. L. Allinger, *J. Org. Chem.*, **27**, 443 (1962).  
 (11) C. A. Coulson and W. T. Dixon, *Tetrahedron*, **17**, 215 (1962).  
 (12) L. C. Snyder, *J. Phys. Chem.*, **66**, 2299 (1962).

**Acknowledgments.**—This work was supported by the Ontario Research Foundation and the National Research Council of Canada.

(13) Department of Chemistry, University of California, Los Angeles 24, Calif.

DEPARTMENT OF CHEMISTRY  
 UNIVERSITY OF OTTAWA  
 OTTAWA 2, ONTARIO, CANADA

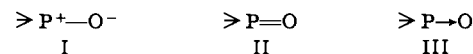
F. A. L. ANET<sup>13</sup>  
 A. J. R. BOURN  
 Y. S. LIN

RECEIVED JUNE 29, 1964

## The Amount of $\pi$ -Bonding in Phosphorus-Oxygen and Sulfur-Oxygen Bonds

Sir:

The amount of  $\pi$ -bonding in phosphorus-oxygen bonds has remained questionable,<sup>1</sup> with various investigators preferring forms I, II, or III. A similar



question applies to sulfur-oxygen bonds. Use of 3d-orbitals in  $\pi$ -bonding at tetrahedral phosphorus seems hard to avoid in ylids considering qualitatively the unusual stability of certain Wittig reagents<sup>2</sup> and quantitatively the analysis of base-catalyzed hydrogen-exchange rates in onium ions of 2nd, 3rd, 4th, and 5th row elements.<sup>3</sup> The dependence of C<sup>13</sup>-H coupling constants on the electronegativity of attached groups<sup>4</sup> offers an ideal way to detect the amount of positive charge on phosphorus or sulfur and therefore the amount of p-d  $\pi$ -bonding in compounds with PO or SO bonds. Table I shows our results most important for the resolution of this problem for phosphine oxides, sulfones, and sulfoxides.

TABLE I  
 C<sup>13</sup>-H COUPLING CONSTANTS

| Compound   | Solvent <sup>a</sup>                                  | <i>J</i> <sup>b</sup> | Compound  | Solvent <sup>a</sup>              | <i>J</i> <sup>b</sup> |
|--|---|-----------------------|---|-----------------------------------|-----------------------|
| (CH <sub>3</sub> ) <sub>3</sub> N                              | Neat  | 131                   | (CH <sub>3</sub> ) <sub>3</sub> P                             | Neat                              | 127                   |
| (CH <sub>3</sub> ) <sub>4</sub> N <sup>+</sup> Cl <sup>-</sup> | D <sub>2</sub> O or CF <sub>3</sub> CO <sub>2</sub> H | 145                   | (CH <sub>3</sub> ) <sub>4</sub> P <sup>+</sup>                | D <sub>2</sub> O                  | 134                   |
| (CH <sub>3</sub> ) <sub>2</sub> NH                             | D <sub>2</sub> O or CF <sub>3</sub> CO <sub>2</sub> H | 143                   | (CH <sub>3</sub> ) <sub>2</sub> P <sup>+</sup> H              | CF <sub>3</sub> CO <sub>2</sub> H | 135                   |
| (CH <sub>3</sub> ) <sub>3</sub> NO                             | D <sub>2</sub> O                                      | 143                   | (CH <sub>3</sub> ) <sub>3</sub> PO                            | D <sub>2</sub> O                  | 129                   |
| (CH <sub>3</sub> ) <sub>2</sub> NOH                            | CF <sub>3</sub> CO <sub>2</sub> H                     | 144                   | (CH <sub>3</sub> ) <sub>2</sub> P <sup>+</sup> OH             | CF <sub>3</sub> CO <sub>2</sub> H | 131                   |
| CH <sub>3</sub> NO <sub>2</sub>                                | Neat  | 148                   | (CH <sub>3</sub> ) <sub>2</sub> S                             | Neat                              | 138 <sup>c</sup>      |
|  |   |                       | (CH <sub>3</sub> ) <sub>2</sub> S <sup>+</sup> I <sup>-</sup> | CF <sub>3</sub> CO <sub>2</sub> H | 146                   |
| CH <sub>3</sub> CON(CH <sub>3</sub> ) <sub>2</sub>             | Neat  | 138                   | (CH <sub>3</sub> ) <sub>2</sub> SO                            | Neat                              | 138 <sup>c</sup>      |
| CH <sub>3</sub> CON(CH <sub>3</sub> ) <sub>2</sub>             | D <sub>2</sub> O                                      | 139                   | (CH <sub>3</sub> ) <sub>2</sub> SO <sub>2</sub>               | D <sub>2</sub> O                  | 139 <sup>c</sup>      |

<sup>a</sup> Where protonated onium ions were studied in CF<sub>3</sub>CO<sub>2</sub>H we may not have complete protonation; these samples were prepared by addition of 1 mole of the neutral substrate to at least 3 moles of CF<sub>3</sub>CO<sub>2</sub>H. <sup>b</sup> Coupling constants determined by linear measurement on an A-60 spectrometer at 250 c.p.s. sweep width; a check of some coupling constants using a frequency counter indicates that these values are probably good to  $\pm 0.5$  c.p.s. <sup>c</sup> The coupling constants for some of the compounds containing sulfur had been reported previously [N. Muller, *J. Chem. Phys.*, **36**, 359 (1964)], but these values are from our measurements.

The large increase in coupling constant in (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup> over (CH<sub>3</sub>)<sub>3</sub>N is due to the greater electronegativity of N<sup>+</sup> compared to  $>N$ ; when the nitrogen is more electronegative, it pulls more p-character into the carbon atomic orbital involved in the CN bond, leaving more s-character in the CH bonds leading to a larger C<sup>13</sup>-H coupling constant.<sup>4</sup> A simple calculation based on the nearly linear relation of s-character to C<sup>13</sup>-H coupling constants<sup>5</sup> indicates that the amount of

- (1) R. F. Hudson in "Advances in Inorganic and Radiochemistry," Vol. 5, Academic Press, New York, N. Y., 1963, pp. 368-377.  
 (2) U. Schoellkopf, *Angew. Chem.*, **71**, 260 (1960).  
 (3) W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **77**, 521 (1955).  
 (4) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 1471 (1959).  
 (5) N. Muller and D. E. Pritchard, *ibid.*, **31**, 768 (1959).