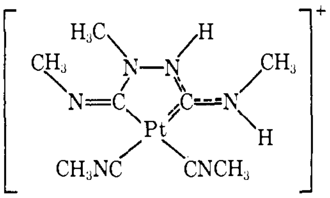
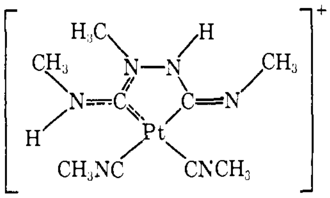
resonance at 4.0 (ri 1) which is assigned to the H_a proton. Although no structure is observed on this latter broad signal, the coupling between H_a and the CH_3 group c has been demonstrated in double resonance experiments. No resonance due to the H_b protons could be observed; the failure to observe these protons could be caused by excessive breadth or by overlap with the phenyl resonances which appear as multiplets centered at 3.1 and 2.6. The nmr spectrum of the analogous complex derived from methylhydrazine is also consistent with the loss of a proton from one of the terminal nitrogens of the chelate, but in this case the spectrum is more complicated because of the presence of two isomers **6a** and **6b** in solution.



6a



6b

Although the structures of the molecules described herein are unusual, they are not unprecedented. The addition of aniline to $PtCl_2(CNMe)(PEt_3)$ to give the related carbene complex $PtCl_2[C(NHMe)NHPh]PEt_3$ has recently been reported.[6] Several examples of insertion of alkyl groups into the triple bond of coordinated isocyanides to give the unit $MC(R)=NR'$ have been reported,[7] but protonation reactions of this latter unit do not appear to have been described. Finally we note that the copper-catalyzed addition of amines and isocyanides to give formamidic acid derivatives[8] may involve nonchelated intermediates with metal coordination similar to that found in **4** or **5**.

Acknowledgment. This research was supported by Grant AM 12182 from the National Institutes of Health and GP12299 from the National Science Foundation.

---

[6] E. M. Badley, J. Chatt, R. L. Richards, and G. A. Sim, *Chem. Commun.*, 1322 (1969).

[7] S. Otsuka, A. Nakamura, and T. Yoshida, *J. Amer. Chem. Soc.*, **91**, 7196 (1969); P. M. Triechel and J. P. Stenson, *Inorg. Chem.*, **8**, 2563 (1969); Y. Yamamoto, H. Yamazaki, and N. Hagihara; *J. Organometal. Chem.*, **18**, 189 (1969).

[8] T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and H. Yoshioka, *Tetrahedron Lett.*, 6121 (1966).

A. Burke, A. L. Balch
Contribution No. 2528, Department of Chemistry
University of California, Los Angeles, California 90024

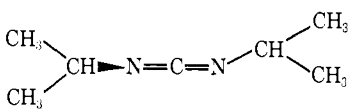
John H. Enemark
Department of Chemistry, University of Arizona
Tucson, Arizona 85721

Received January 29, 1970

Energy Barrier of Racemization in Diisopropylcarbodiimide

Sir:

Carbodiimides are expected to exhibit the same molecular dissymmetry as do appropriately substituted allenes.[1] Although allenes have been resolved, first[2] in 1936, attempts to demonstrate experimentally the chirality of carbodiimides have been unsuccessful[3,4] except for one questionable claim.[5] Gordon and Fischer[6] using the INDO molecular orbital method calculated the thermodynamically most stable geometry of carbodiimide and difluorocarbodiimide. The ground state, according to these calculations, is the intuitively favored dissymmetric geometry with the substituents in perpendicular planes which intersect along the N=C=N axis. The calculated energies of activation for thermal racemization of carbodiimide and difluorocarbodiimide are 8 and 22 kcal/mol, respectively. Since the calculations are thought to give barriers which are slightly too high,[6] the barrier in carbodiimide is probably no higher than 8 kcal/mol. Thus, attempts to prepare optically active alkyl- and aryl-substituted carbodiimides will not be possible because of rapid racemization at room temperature. Later *ab initio* SCF calculations by Lehn and Munsch[7] agree with the results of Gordon and Fischer,[6] while recent INDO calculations[8] on dimethylcarbodiimide indicate a minimum energy for a valence angle $CH_3—N=C$ of 90°.



I

We now report nmr data on the rate of racemization in diisopropylcarbodiimide (I). The methyl groups of either isopropyl are diastereotopic and thus should show different chemical shifts if racemization is slow on the nmr time scale. The 240-MHz[9] proton resonance spectrum of diisopropylcarbodiimide in 1:1 vinyl chloride–dichlorofluoromethane solution shows at −130° and above a doublet (J = 6.5 Hz) for the methyl protons owing to coupling to the adjacent methine proton (Figure 1a). On lowering the temperature the doublet broadens greatly (−140°, Figure 1b) and below −145° (Figure 1c) becomes a 1:2:1 three-

---

[1] H. Fischer, "The Chemistry of Alkenes," S. Patai, Ed., John Wiley & Sons, Inc., London, 1964, p 1061.

[2] P. Maitland and W. H. Mills, *J. Chem. Soc.*, 987 (1936).

[3] L. J. Rolls and R. Adams, *J. Amer. Chem. Soc.*, **54**, 2495 (1932).

[4] J. C. Jochims, unpublished results.

[5] K. Schlögl and M. Mechter, *Angew. Chem. Int. Ed. Engl.*, **5**, 596 (1966). These authors report the partial resolution of diferrocenylcarbodiimide. However, since the maximum optical rotation observed, $[\alpha]_D$ −4.8° (c 0.3, benzene), is very small, the possibility that the rotation was due to an impurity must be considered. Unfortunately, the authors did not report any experimental test to show that the carbodiimide itself was optically active. Attempts by Jochims[4] to resolve carbodiimides have sometimes given products with a low rotation, but since the rotations remained after transformation of the carbodiimides into ureas, no actual resolutions had occurred.

[6] M. S. Gordon and H. Fischer, *J. Amer. Chem. Soc.*, **90**, 2471 (1968).

[7] J. M. Lehn and B. Munsch, *Theoret. Chim. Acta.*, **12**, 91 (1968).

[8] D. R. Williams and R. Damrauer, *Chem. Commun.*, 1380 (1969).

[9] Details of the spectrometer, which makes use of a Magnion superconducting solenoid, will be published elsewhere; *cf.* F. A. L. Anet, paper presented at the Tenth Experimental NMR Conference, Pittsburgh, Feb 1969.

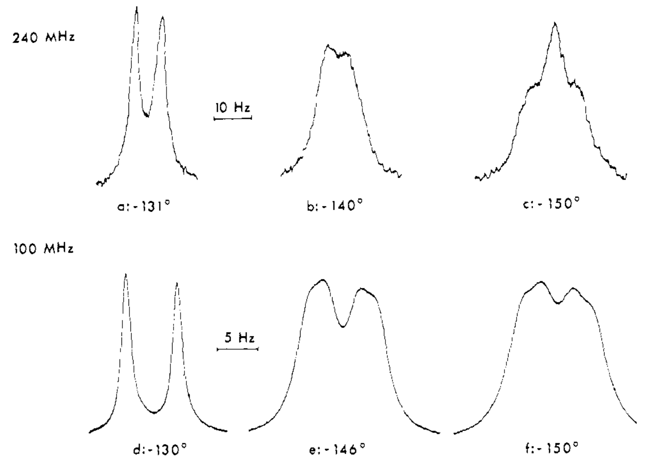


Figure 1. Spectra (240 and 100 MHz) of the methyl protons of diisopropylcarbodiimide at various temperatures.

line spectrum arising from two overlapping doublets with a chemical shift difference of about 6 Hz.

At 100 MHz the different chemical shifts could be seen through the appearance of inflection points (Figure 1f) only by a careful investigation of a more dilute sample in a solvent of lower viscosity, 1:1 vinyl chloride–chlorodifluoromethane.[10] These inflections disappear at −146° (Figure 1e) and a doublet with a coupling constant of 6.5 Hz is obtained at −130° (Figure 1d).

These results clearly demonstrate the dissymmetry of diisopropylcarbodiimide.[11] Chemical shift differences of similar magnitude have been reported for diastereotopic substituents on allenes.[12] The free energies of activation calculated from the coalescence temperature and the chemical shift differences are, at 240 MHz, 6.7 ± 0.2 kcal/mol, and at 100 MHz, 6.6 ± 0.3 kcal/mol; these values agree with theoretical predictions.[6,7,13]

Concerning the racemization mechanism, Gordon and Fischer[6] calculated that, for carbodiimide, rotation through the *trans* form, whereby the dihedral angle of the substituents increases from 90 to 180°, is favored over nitrogen inversion by 0.3 kcal/mol and suggested that the actual mechanism was probably a combination of rotation and inversion. Our present study does not give any information on the mechanism of racemization.

Acknowledgment. This work was supported by the U. S. Public Health Service.

[10] Varian HA-100 spectrometer.

[11] Although the experimental results can be interpreted in terms of restricted rotation about the N–C single bond, we consider this possibility to be very unlikely.

[12] M. L. Martin, R. Mantione, and G. J. Martin, *Tetrahedron Lett.*, 4809 (1967).

[13] The errors given for the ΔF's are based on estimated maximal errors in the temperature of ±3° and an estimated uncertainty in chemical shift differences of ±1 Hz.

[14] On leave from Max-Planck-Institut für Medizinische Forschung, Heidelberg, Germany.

[15] Carbodiimides. V. For part IV see J. C. Jochims, *Chem. Ber.*, **101**, 1746 (1968).

F. A. L. Anet, J. C. Jochims,[14,15] C. H. Bradley
Contribution No. 2450, Department of Chemistry
University of California, Los Angeles, California 90024

Received January 20, 1970

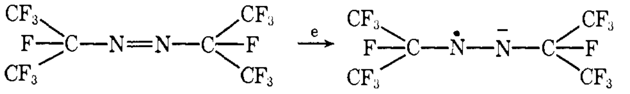
Electron Spin Resonance of Perfluoroazoalkane Radical Anions[1]

Sir:

Further investigations into the factors influencing the magnitude of β-fluorine hyperfine coupling in radical anions[2–5] have led to a study of the electron spin resonance (esr) spectra of perfluoroazoalkane radical anions. Perfluoroazoethane[6] is easily reduced on a platinum electrode at an applied voltage of −0.25 V in dry acetonitrile containing tetraethylammonium perchlorate.[7] An intense signal was produced immediately consisting of five groups of lines separated by approximately 35 G which could be further resolved into a total of 204 lines. Since first-order fluorine hyperfine coupling ($I = {}^1/_2$) can only account for 175 lines, support for second-order coupling was sought by inspection of a well-resolved spectrum produced at a very long time scan (250 G in 100 min) and recorded on a high gain recorder. Very good correlation was found with a second-order analysis[8] if the 35.25-G second-order coupling is assigned to four equivalent (β) fluorines and the 7.72- and 4.22-G first-order couplings are assigned to two equivalent nitrogen atoms and six equivalent (γ) fluorine atoms, respectively. In this analysis a total of 315 lines are predicted[8] ((5 × 7 × 1) + (5 × 7 × 2) + (5 × 7 × 3) + (5 × 7 × 2) + (5 × 7 × 1) = 315).

$$\mathrm{CF_3CF_2N{=}NCF_2CF_3} \xrightarrow{\mathrm{e}} \mathrm{CF_3CF_2\dot{N}\bar{N}CF_2CF_3}$$

The production of perfluoro-2-azopropane radical anion was also accomplished by electrolytic reduction of perfluoro-2-azopropane[9] at −3.0 V in acetonitrile. The spectrum consists of three groups of lines separated by approximately 60 G. Forty-five peaks in a symmetrical pattern were resolved in each side group. Approximately twice this number were resolved in the central group. The spectrum is consistent with a 62.45-G coupling from two equivalent fluorine atoms with a second-order splitting of 1.43 G. Further splitting of 7.81 G from two nitrogen atoms and 4.79 G from twelve (γ) fluorine atoms accounts for the splitting within each of the three groups of lines.



[1] This work was supported by AFOSR(SRC)-OAR U.S.A.F. Grant No. 1069-66 and the Petroleum Research Fund administered by the American Chemical Society.

[2] E. G. Janzen and J. L. Gerlock, *J. Amer. Chem. Soc.*, **89**, 4902 (1967).

[3] E. G. Janzen and J. L. Gerlock, *J. Phys. Chem.*, **71**, 4577 (1967).

[4] J. L. Gerlock and E. G. Janzen, *J. Amer. Chem. Soc.*, **90**, 1652 (1968).

[5] J. L. Gerlock and E. G. Janzen, *J. Phys. Chem.*, **72**, 1832 (1968).

[6] Perfluoroazoethane was prepared by the reaction of silver difluoride with trifluoroacetonitrile according to J. K. Ruff, *J. Org. Chem.*, **32**, 1675 (1967), and references therein.

[7] A platinum cathode inserted into the flattened region of a quartz vacuum electrolysis cell was used directly in an esr cavity.

[8] R. W. Fessenden, *J. Chem. Phys.*, **37**, 747 (1962).

[9] Perfluoro-2-azopropane was prepared by allowing silver difluoride to react with hexafluoroacetone imine at room temperature in a closed system. This product was separated from the azine, $\mathrm{(CF_3)_2CNNC(CF_3)_2}$, by slow vacuum line fractionation and identified by vapor density molecular weight measurement and fluorine-19 nmr and ir spectroscopy. The purity was checked by vpc. The esr spectrum of the tetrakis(trifluoromethyl)azine radical anion was also obtained. Further details will be reported at a later date.