In the case of carbanions, it is known that the cyclopropyl carbanion has a much higher barrier to inversion that its open-chain analogs[9] and that the vinyl anion also retains its geometry tenaciously (estimated barrier to inversion >25–35 kcal/mole[10]). This evidence refers, however, not to the free anions but to their lithium derivatives; one cannot therefore be sure that we are right in predicting that the barriers in carbanions are much higher than in their corresponding amines, although this certainly does seem to be the case.

(9) See H. M. Walborsky, *Record Chem. Prog.*, **23**, 75 (1965).
(10) S. I. Miller and W. G. Lee, *J. Am. Chem. Soc.*, **81**, 6313 (1959).

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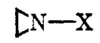
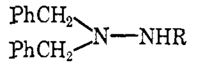
Rotation–Inversion Barriers in Hydrazines[1]

Sir:

We wish to report the discovery of considerable barriers to rotation and/or inversion in some simple hydrazines. Previous work has shown the existence of surprisingly large barriers to rotation about P–N bonds in aminophosphines[2] and N–As bonds in aminoarsines,[2a] and similar rotational barriers have been observed about N–S[3] and N–O[4] bonds. These barriers are much too large to be due to conformational effects of the kind that operate in ethane; they must be attributed to lone-pair interactions. On this basis one might expect to find comparable barriers to rotation about the N–N bond in hydrazines. Barriers to rotation have indeed been reported for di- and tetraacylhydrazines, where both nitrogen atoms are of amide type,[5] and in hydrazones,[6] triazines,[7] and tetrazines.[8] Here, however, one might expect π bonding or steric effects to lead to enhanced barriers to rotation; no measurements have as yet been reported for hydrazines of simpler types.

A further complicating factor is the possibility of an enhanced barrier to inversion of nitrogen in compounds where nitrogen is attached to another atom carrying unshared electrons. Thus the barriers to inversion in aziridine derivatives I, where X is NH_2 or chlorine, are very much greater than in aziridine itself,[9] and indeed Roberts, *et al.*,[4b] attributed the barriers in simple hydroxylamines to inversion rather than rotation. It is true that the barrier to inversion in hydrazine has been reported[10] to be much lower than that for ammonia; this, however, is at variance with the evidence from N-aminoaziridine[9] and also with SCF MO calculations which predict a barrier height in hydrazine of ~10 kcal/mole.[11]


I


II, R = H
III, R = 2, 4-dinitrophenyl
IV, R = picryl
V, R = 2-pyrimidyl

We have now examined the nmr spectra[12] of 1,1-dibenzylhydrazine (II), and of its 2,4-dinitrophenyl (III), picryl (IV), and 2-pyrimidyl (V) derivatives. All of the spectra showed a dependence on temperature that indicated significant barriers to inversion and/or rotation.

Table I. Spectral Data and Free Energy of Activation ($\Delta G^{\ddagger}_c$) Estimated at the Coalescence Temperature (T_c)

Compd	Solvent	$\Delta\nu_{AB}{}^a$ (at T), Hz	J_{AB}, Hz	T_c, °C	$\Delta G^{\ddagger}_c$, kcal/mole
II	CCl_3F-$CH_2Cl_2{}^b$	~50		−95	~8.5
III	$CDCl_3$	27.0 (0°)	12.8	59	16.6
IV	$CDCl_3$	12.3 (0°)	12.8	50	16.2
V	$CDCl_3$	29.7 (−60°)	13.3	−38	11.5

[a] At 100 MHz. [b] ~3:1.

In the case of II, the benzyl protons must be equivalent unless the adjacent nitrogen atom is pyramidal and inverts slowly, effectively forming an asymmetric center. At room temperature the corresponding nmr signal was a sharp singlet, but below −80° in dichloromethane–fluorotrichloromethane the line broadened rapidly and at −104° had separated in two broad peaks. Although the limiting low-temperature spectrum was not attained, a reasonable estimate of the free energy of activation at the coalescence temperature (−95°) could be made (Table I). The barrier is in good agreement with that calculated theoretically; it seems clear that the value (3.5 kcal/mole) reported[10] for hydrazine itself must be incorrect.

In the case of the substituted dibenzylhydrazines III–V, the signal for the benzylic protons at low tem-

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(3) H. J. Jacobsen and A. Senning, *Chem. Commun.*, 617 (1967); M. Raban, F. B. Jones, Jr., and G. W. J. Kenney, Jr., *Tetrahedron Letters*, 5055 (1968); J. M. Lehn and J. Wagner, *Chem. Commun.*, 1298 (1968).
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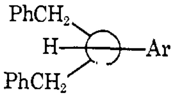
(5) B. H. Korsch and N. V. Riggs, *Tetrahedron Letters*, 5897 (1966); G. J. Bishop, B. J. Price, and I. O. Sutherland, *Chem. Commun.*, 672 (1967); A. Foucand and R. Roudant, *Compt. Rend., Ser. C*, **266**, 726 (1968).
(6) A. Mannschreck and U. Koelle, *Tetrahedron Letters*, 863 (1967).
(7) N. P. Marullo, C. B. Mayfield, and E. M. Wagener, *J. Am. Chem. Soc.*, **90**, 510 (1968).
(8) W. M. Tolles, D. W. Moore, and W. E. Thun, *ibid.*, **88**, 3476 (1966).
(9) S. J. Brois, *Tetrahedron Letters*, 5997 (1968); *J. Am. Chem. Soc.*, **90**, 506, 508 (1968).
(10) T. Kasuya and T. Kojima, Proceedings of the International Symposium on Molecular Structure and Spectroscopy, Tokyo, 1962, p C204; *Chem. Abstr.*, **61**, 2616*d* (1964).
(11) M. J. S. Dewar and M. Shanshal, *J. Am. Chem. Soc.*, **91**, 3654 (1969).
(12) The spectra were measured by Mr. E. J. Burshnick on a Varian HA-100 spectrometer using TMS as internal lock, with 5–10% (w/v) solutions.

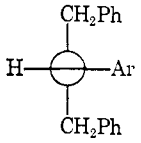
peratures was a typical AB quartet. On raising the temperature, the quartet collapsed reversibly to a singlet in the manner characteristic of protons undergoing a critical rate site exchange on the nmr time scale. Free energies of activation were estimated at the coalescence temperature (T_c) from eq 1 and the Eyring equation;[13] these values and the various nmr parameters are listed in Table I.

$$k_c = \pi(\Delta\nu_{AB}^2 + 6J_{AB}^2)^{1/2}2^{-1/2} \qquad (1)$$

If the benzyl groups were nonequivalent at lower temperatures, the methylene protons in each group remaining equivalent, the spectrum would be a doublet, not a quartet. The observed spectrum therefore indicates that the methylene protons must be nonequivalent. However the benzyl groups *are* equivalent since otherwise one would observe two AB quartets, not one. These observations show either that rotation about the N–N bond must be rapid or that the compounds have the conformation VI where the imino nitrogen is either planar or rapidly inverting (so that it is planar on an average). The nonequivalence of the benzyl protons could then be due either to slow inversion of the adjacent nitrogen atom or slow rotation about the N–N bond coupled with rapid inversion (or planarity) of both nitrogens; in the latter case the structure would be effectively VII.



VI



VII

There is another conceivable way in which asymmetry could arise. In the case of picryl, steric hindrance will probably prevent the phenyl-N-N system from being coplanar. Since rotation about the C–N bond in picramides seems to require considerable activation,[14] the molecule could then exist in two enantiomeric forms, depending on the chirality of the ring relative to the system $(PhCH_2)_2N-NH-C$. Indeed, a second temperature-dependent process was observed in the spectrum of IV in the same temperature range. At 0° the two picryl protons appeared as an AX system ($\Delta\nu_{AX}$ = 57.3 Hz; J_{AX} = 2.7 Hz)[15] which coalesced at 58° to a broad A_2 system; the corresponding value for $\Delta G^{\ddagger}$ (16.2 kcal/mole) was essentially identical with that for coalescence of the benzyl protons, and similar barriers have been observed[14] in other picramides. This explanation cannot, however, apply in the case of III or V since in both cases the Ar–N–N system can be coplanar; the measured barrier here must refer to nitrogen inversion–rotation.

The fact that the barrier in II is greater than that in a simple amine can be attributed to enhanced repulsion between the nitrogen lone pairs when one of them occupies a p AO instead of a sp^3 hybrid AO; such a situation exists in the transition state for inversion. If both nitrogen atoms were planar, repulsion would then presumably be still greater. Any tendency to coplanarity of one nitrogen atom in hydrazine should therefore tend to increase the barrier to inversion at the other nitrogen, since inversion will involve a transition state in which both nitrogen atoms are coplanar.

One might also expect coplanarity of one or both nitrogen atoms in hydrazine to increase the barrier to rotation for the same reason, the lone-pair repulsions in the transition state for rotation being augmented if the electrons occupy p or π orbitals.

On either basis one could attribute the enhanced barriers in III and V to a resonance interaction between the electrophilic aromatic ring and the imino nitrogen, thus tending to make the nitrogen atom more nearly coplanar than that in II and the barrier to inversion or rotation correspondingly greater.

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[14] J. Heidberg, J. A. Weil, G. A. Janusonis, and J. K. Anderson, *J. Chem. Phys.*, 41, 1033 (1964).

[15] The overlapping NH signal was removed by deuteration.

Spin Delocalization in Aromatic Complexes of Transition Metals

Sir:

Recently the weaknesses of the Levy–Orgel[1] mechanism for spin delocalization in the metallocenes has been recognized,[2,3] and alternative mechanisms[3–5] have been postulated to explain the observed contact shift data. Rettig and Drago[3] have made a thorough analysis of the data and have proposed a molecular orbital model which is able to explain the observed contact shifts by invoking three competing mechanisms: (1) a pseudocontact mechanism which appears to be negligible except for perhaps chromocene and ferricinium ion; (2) a π mechanism which involves atomic exchange polarization and becomes more important as one goes from vanadocene to nickelocene; and (3) a σ mechanism which delocalizes unpaired spin density directly onto the protons of the ring. In detailed semiempirical calculations[3,6] several workers have noted the importance of σ bonding in what have primarily been considered "π complexes." In fact our calculations show that σ delocalization of spin completely swamps the π-polarization effects for vanadocene and is of approximately equal importance in nickelocene. Fritz, *et al.*,[5] have concurred with our proposal of competing mechanisms but suggest that *direct overlap* of metal orbitals with ring protons of the cyclopentadiene is the dominant mechanism for direct spin delocalization. This mechanism is said to place spin directly on the ring protons without altering the sign of the spin density and leads to the large downfield shifts observed in vanadocene, for example. These authors[5] have suggested this model also accounts for the delocalization of unpaired spin in the series of benzene complexes.

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