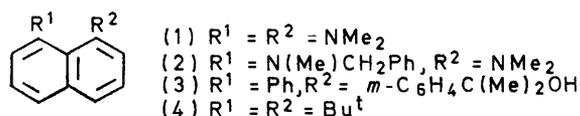


peri-Interactions in Naphthalene Derivatives. Low Temperature Nuclear Magnetic Resonance Study of 1,8-Bisdimethylamino- and 1-Benzylmethylamino-8-dimethylamino-naphthalene

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The *N*-methyl signal of 1,8-bisdimethylaminonaphthalene (1) separates into a doublet at -120° , while for 1-benzylmethylamino-8-dimethylaminonaphthalene (2) a different process causes non-equivalence of the NMe_2 and CH_2Ph groups below -8° . The nature of these processes is discussed and barriers are reported.

THERE has been considerable interest in 1,8-bisdimethylaminonaphthalene (1) since one of us reported¹ its high basicity. The conformation about the *peri*-bonds in the crystal has now been determined² by X-ray crystallography, and this leads to the question of rotation about



these bonds. This topic is particularly interesting since a high barrier to rotation of *peri*-groups has been found³ for (3) while by contrast an unusually low barrier has been found⁴ for (4), in both cases on the basis of a temperature-dependent n.m.r. spectrum. Indeed in the original report¹ it was noted that in (2) the methylene group signal changes from a singlet at room temperature to an AB quartet at -30° . We now report further on the temperature dependence of the n.m.r. spectrum of both (1) and (2).

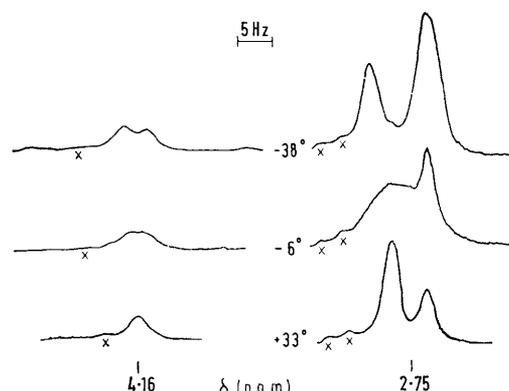
RESULTS

The 100 MHz n.m.r. spectrum of (1) in CF_2Cl_2 solution at ambient probe temperature shows a singlet absorption at δ 2.77 for the *N*-methyl groups, and an apparent ABC spectrum between δ 6.8 and 7.3 for the aromatic protons (analysed elsewhere). Below -70° the *N*-methyl singlet broadens and splits below -120° to a 1:1 doublet with a relative shift 25.9 Hz at 100 MHz centred at δ 2.74 at -133° . At this temperature the aromatic hydrogens show line broadening but no changes that could be associated with a conformational equilibrium. The free energy of activation for the process manifested by the change in the *N*-methyl signals is 7.5 ± 0.2 kcal mol⁻¹ at -120° .

The upfield part of the n.m.r. spectrum of (2) at several temperatures is shown in the Figure. At ambient temperature in deuteriochloroform solution, the spectrum comprises two signals of relative intensity 2:1 at δ 2.78 and 2.73 respectively for the *N*-methyl groups, a singlet at δ 4.16 for the methylene group and a complex spectrum between δ 6.80 and 7.45 for the various aromatic hydrogen atoms. As the temperature is lowered below $+10^\circ$, the methylene signal and the more intense of the *N*-methyl signals begin to broaden. At -38° , the methylene signal appears as an AB quartet, δ_A 4.12, δ_B 4.22 (J_{AB} 14.4 Hz) while the downfield *N*-methyl signal is now a doublet, the upfield part of which is isochronous with the temperature-

independent *N*-methyl signal, so that the *N*-methyl region appears as a 1:2 doublet at δ 2.83 and 2.74. The coalescence temperature for the methylene signal is *ca.* -2° , and for the *N*-methyl signal is *ca.* -8° whence the free energy of activation for the conformational process giving rise to these spectral changes is 13.7 ± 0.4 kcal mol⁻¹.

Similar behaviour was observed for a CF_2Cl_2 solution of (2) but no evidence for further conformational changes was



Part of the n.m.r. spectrum of (2) at various temperatures:
x = impurities

observed for this solution on cooling to -120° , though increased broadening might have masked further changes in the spectrum.

DISCUSSION

The spectral changes for (1) and (2) suggest that conformational processes are taking place, but before discussing these, the most stable conformation for each molecule must be decided. In the case of (1) we assume that this is the same in solution as in the crystal² and is as shown in (5). This conformation (point group C_2) is in accord with the n.m.r. spectrum at -135° and can be best understood as a compromise arrived at by the interaction of several destabilising factors (ring twisting and distortion, lone-pair-lone-pair repulsions, lone-pair-hydrogen and hydrogen-hydrogen repulsions) and a stabilising factor (lone-pair- π overlap). If (2) adopts a related conformation, there are two possibilities, (6) and (7). These are not equivalent, but, even at the lowest temperature, we saw no sign of n.m.r. signals of different intensity, so we assume that one of these

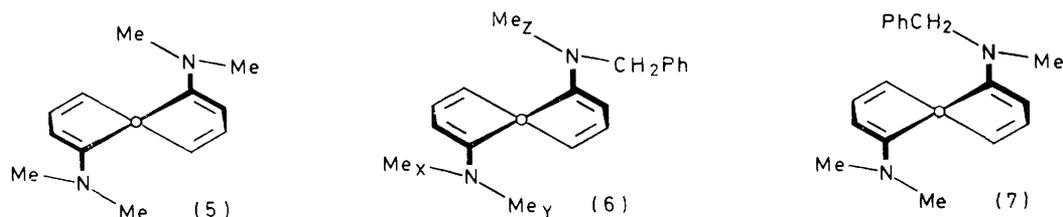
¹ R. W. Alder, P. S. Bowman, W. R. S. Steele, and D. R. Winterman, *Chem. Comm.*, 1968, 723.

² E. Einspahr, J. B. Robert, R. E. Marsh, and J. D. Roberts, *Acta Cryst.*, 1973, **29B**, 1611.

³ H. O. House and R. W. Bashe, *J. Org. Chem.*, 1967, **32**, 784; H. O. House, W. J. Campbell, and M. Gall, *ibid.*, 1970, **35**, 1815.

⁴ J. E. Anderson, R. W. Franck, and W. L. Mandella, *J. Amer. Chem. Soc.*, 1972, **94**, 4608.

conformers is substantially more stable than the other. Models suggest that this is probably (6) and indeed this seems to fit the n.m.r. spectrum best. The methyl groups Y and Z in (6) being out of the plane of the ring, are expected to be at higher field than methyl group X



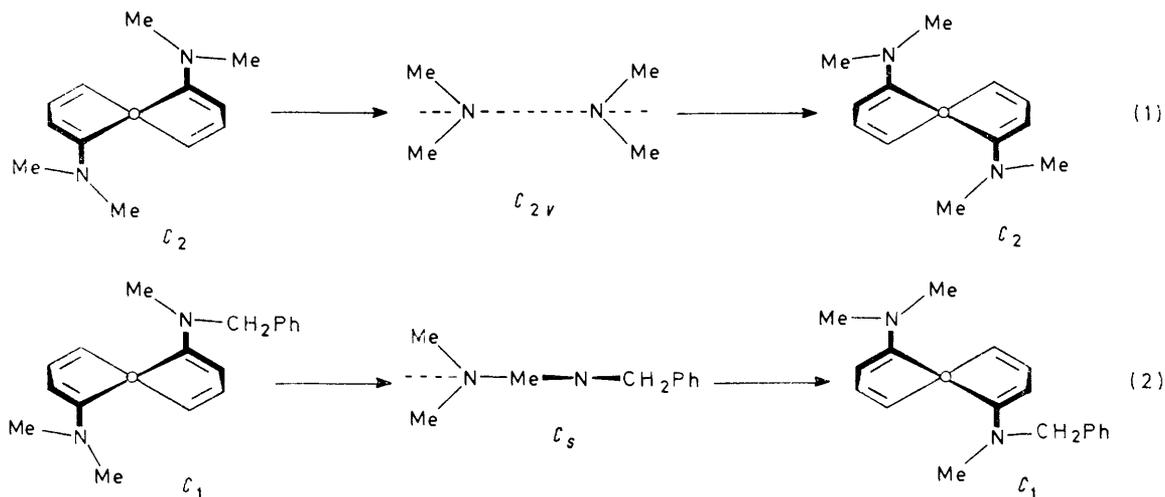
which is in the maximum deshielding zone of the aromatic ring current, so it can be argued that Me_Z should be at higher field than the mean of Me_X and Me_Y , and this is in fact observed in the room temperature n.m.r. spectrum of (2). The presence of as much as 10% of (7) at equilibrium cannot be excluded on the basis of the low temperature n.m.r. spectra recorded.

The symmetrical nature of the spectral changes suggest narcissistic processes⁵ (interconversion of object and mirror image). These are shown in equations (1) and (2), and in each case the pathway shown is the most

in terms of the conventional, 'simple' process of nitrogen inversion, bond rotation, and ring flipping⁴ is unsatisfactory, since it seems quite likely that each of these processes, operating alone on compounds (1) or (2) leads to a conformation which is not at an energy

minimum. Even if the pathway is non-synchronous and consists of a sequence of steps *via* secondary energy minima, it is unlikely that these steps are simple nitrogen inversion, *etc.*

It should be emphasised that the difference in barriers between compounds (1) and (2) is not taken to represent a difference in the process in these two molecules. Both compounds will have in the conformational equilibration cycle, states similar to the C_{2v} state of (1) and similar to the C_s state of (2). By virtue of its substitution pattern, changes in the spectrum of (2) are observed when



easily envisaged one, the synchronous (Salem's terminology⁵).

The symmetrical midpoint forms may represent the transition state but need not. These midpoint forms imply a specific degree of rotation about Ar-N bond, flipping of Ar-N bond, specifically into the mean plane of the molecule, and an unspecified amount of nitrogen inversion. An infinite variety of non-synchronous pathways are conceivable and cannot be excluded on experimental grounds. Extensive discussion of the plausibility of these pathways does not seem profitable, especially in the absence of force-field or other calculations and we merely comment that the synchronous pathways do seem quite likely to be minimum energy pathways in both cases. We would however like to point out that dissection of the conformational changes

passage through a conformation close to the C_s form become slow on the n.m.r. time scale and the barrier to this passage is 13 kcal mol⁻¹. Molecules of (1) are expected to experience a similar barrier to passage through an equivalent C_s form, but this has no effect on its n.m.r. spectrum. By virtue of its substitution pattern, it is only when passage through a conformation close to the C_{2v} form becomes slow that (1) shows changes in its n.m.r. spectrum, and the barrier to this process is 7.5 kcal mol⁻¹.

Finally we note that the C_{2v} form of (1), which presumably maximises lone-pair-lone-pair repulsions is at least 7.5 kcal mol⁻¹ higher in free energy than (5). This suggests that a rigid molecule with the C_{2v} conformation

⁵ L. Salem, J. Durup, C. Bergeron, D. Cazes, X. Chapuisat, and H. Kagan, *J. Amer. Chem. Soc.*, 1970, **92**, 4472.

would have still more extreme properties than (1) and be, for example, a considerably stronger base.

EXPERIMENTAL

1,8-Bisdimethylaminonaphthalene (1).—This was obtained from Aldrich and was purified by sublimation at 100° and 0.1 Torr, to give crystals, m.p. 47—48°.

1-Dimethylamino-8-methylaminonaphthalene.—This was originally obtained by chromatography of the product of incomplete methylation of 1,8-diaminonaphthalene. A more convenient preparation is by thermal decomposition of the HNCS salt of (1). Compound (1) was dissolved in dilute acetic acid and aqueous sodium thiocyanate added. The precipitate was dried and recrystallised from MeOH, m.p. 220—224° (decomp.). Thiocyanate (13 g) was heated at 215—225° for 2 h under nitrogen and the dark product co-distilled with ethane-1,2-diol. A light petroleum extract

was washed with pH 7 buffer to remove (1), dried, and evaporated to give almost pure 1-dimethylamino-8-methylaminonaphthalene (5 g). The compound may be purified by conversion to its picrate, m.p. 163—164°, and recrystallisation of the liberated base at -80° from light petroleum, m.p. 29—30°.

1-Benzylmethylamino-8-methylaminonaphthalene (2).—1-Dimethylamino-8-methylaminonaphthalene was warmed with benzyl bromide and the resulting solid washed with benzene to remove the excess of benzyl bromide. The salt was dissolved in methylene chloride and shaken with sodium hydroxide solution to give the free base, obtained as a pale yellow oil.

N.m.r. spectra were measured as described previously.⁶

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⁶ J. E. Anderson and H. Pearson. *Chem. Comm.*, 1971, 871.