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SUBSTITUENT EFFECT ON TORSIONAL BARRIERS IN N,N'-DIBENZYLHYDRAZOBENZENES.

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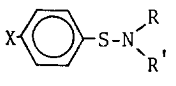
Summary: Substituted hydrazobenzenes were prepared and their barriers to rotation measured by DNMR spectroscopy and correlated with σ^- substituent constants with a reaction constant $\rho_{300} = -1.09$.

Hydrazines belong to a general class of compounds containing a single bond between two heteroatoms, and therefore possessing adjacent lone pairs of electrons. Several chemical properties are common to and characteristic of the class, such as their conformational preference (the gauche effect), high barriers to torsion about the central bond, as well as enhanced nucleophilic activity (the α effect). The present study is part of our continued effort to better understand the chemistry of these compounds.[1] In particular, the effect of substituents on rotational barriers in various member groups of the general class of compounds has not been fully understood. In arenesulfenamides (1), a linear increase of torsional barriers with increasing electron withdrawing power of the substituents (Hammett σ constants) was found.[2] In the analogous substituted hydroxylamines (2), the trend in substituent effects on torsional barriers was not so well defined.[3] Comparison with another member group of compounds seemed desirable.



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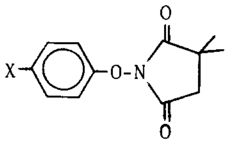

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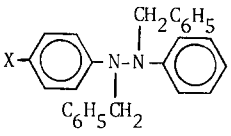
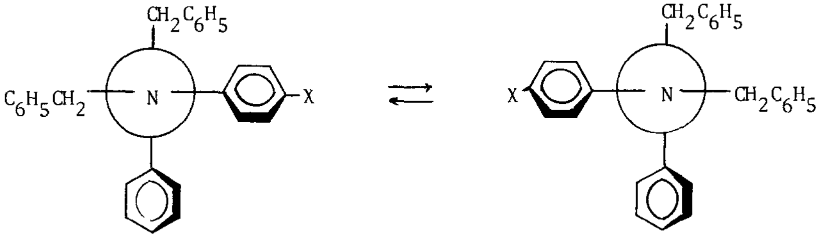


3

3a, X = H
3b, X = OCH_3
3c, X = CH_3
3d, X = Cl
3e, X = CN

para-Substituted N,N'-dibenzylhydrazobenzenes (3) were synthesized by sodium reduction of the corresponding azobenzenes followed by alkylation of the disodio-derivatives with benzyl chloride, as described in the literature.[4] Their ambient temperature 270 MHz proton nmr spectra consist of two singlets for the different methylene groups (with the exception of the symmetric 3a) in the region 4.6-4.7 ppm. At lower temperatures these signals broaden and split until at the slow exchange limit two partially overlapping AB quartets are observed, due to the diastereotopic protons in each methylene group. These protons undergo a topomerization process within each one of the prochiral benzyl groups, in which either nitrogen inversion or N-N bond rotation might be the slow, rate determining step. Dewar and Jennings have shown that in various alkylhydrazines rotation is the dominant rate process.[5] In our case nitrogen inversion should be even faster relative to rotation than in Dewar's study, since conjugation of the nitrogen lone pairs with the aromatic rings tends to flatten the nitrogen pyramid and lower the inversion barrier. Hence the rate process monitored by DNMR must be N-N torsion. Under these conditions of rapid nitrogen inversion the average ground state conformation can be represented by the chiral Newman projection **4** and its enantiomer $\overline{\mathbf{4}}$.



4 $\overline{\mathbf{4}}$

The first order rate constants for torsion were obtained by matching experimental spectra with computer generated spectra using a program designed for two overlapping AB quartets. The free energies of activation were obtained using the Eyring equation. The results are shown in the Table.

The barriers were correlated with σ^- substituent constants (Figure). This correlation was significantly better (R = 0.998) than with Hammett σ constants (R = 0.971), providing evidence for a direct resonance interaction between the nitrogen lone pairs and the aromatic π system. The analysis furnishes a Hammett reaction constant $\rho_{300} = -1.09$,[6] which is substantial for a case in which formal charges are involved in neither ground nor transition states.

The substituent effect is similar to that found in sulfenamides **1**,[2] suggesting that a similar mechanism operates in both systems. The mechanism based on four electron interactions[1a] would require that the torsional barrier for **2a**, the symmetrically substituted hydrazine, be the highest in the series, with a nonlinear Hammett relationship. The results do not agree with this expectation. On the other hand, the "electrosteric" effect proposed recently to account for substituent effects in series **1**,[7] seems to be supported by the present results. However, while in **1** substitution of both <u>ortho</u> positions of the phenyl ring drastically lowers the barriers, as required by the electrosteric effect, this is <u>not</u> the case in hydrazines, where $(PhCH_2)_2NNH$(2,4,6-trinitrophenyl) has practically the same barrier (<u>ca</u>. 16.5 Kcal/mol) as the 2,4-dinitro substituted analogue,[5] indicating some difference in the mechanisms for series **1** and **3**.

Table: 270 MHz DNMR Data for Series **3**.

Compd	X	MP,°C	$\Delta\nu(1)$ Hz[a]	J(1), Hz[b]	$\Delta\nu(2)$, Hz[a]	J(2), Hz[b]	T_1 °K[c]	$\Delta G^{\ddagger}$ [d]
3a	H	121-2	43.4	16.1	—	—	290	14.2
3b	CH_3O	108-9	41.3	17.1	36.0	16.0	265	13.1
3c	CH_3	112-3	40.4	16.5	44.2	16.9	281	13.9
3d	Cl	111-2	38.8	16.7	42.3	16.9	290	14.4
3e	CN	157.5	46.0	17.0	32.0	16.3	318	15.8

a. Extrapolated to T_1 from low temperature values. b. Measured at the slow exchange limit. c. Temperature at which exchange broadening is maximal (approx. coalescence). d. Kcal/mol.

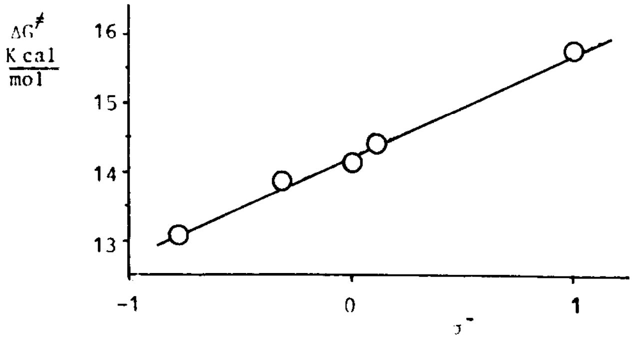


Figure: Hammett plot of rotational barriers for series **3**.

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References and Notes

1. (a) D. Kost, A. Zeichner, and M.S. Sprecher, *J. Chem. Soc. - Perkin II*, 317 (1980);
   (b) D. Kost and M. Raban, *Prog. in Theoret. Org. Chem.*, **2**, 20 (1977).

2. M. Raban and F.B. Jones, Jr., *J. Am. Chem. Soc.*, **93**, 2692 (1971).

3. D. Kost and E. Berman, *Tetrahedron Lett.*, 1065 (1980).

4. J.W.B. Reesor and G.F. Wright, *J. Org. Chem.*, **22**, 375 (1957).

5. M.J.S. Dewar and W.B. Jennings, *J. Am. Chem. Soc.*, **95**, 1562 (1973).

6. Using Raban's temperature independent Hammett analysis,[2] calculated for 300°K.

7. M. Raban and G. Yamamoto, *J. Am. Chem. Soc.*, **101**, 5890 (1979).

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