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COMPARISON OF THE CONFORMATION IN THE CRYSTAL AND IN SOLUTION OF 1-(NITROMETHYL)-3-PHENYLPHTHALAN (1a)

Robert A. Smith, Richard G. Parker, and John D. Roberts
Gates and Crellin Laboratories of Chemistry (1b)
California Institute of Technology
Pasadena, California 91109, U.S.A.

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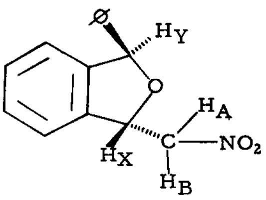
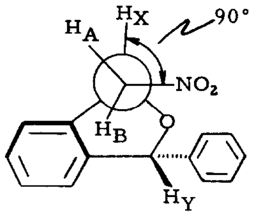
In connection with the stereochemical problem posed by 1,3-disubstituted phthalans, we have determined the crystal structure of trans-1-(nitromethyl)-3-phenylphthalan, I (2). In the crystal, the dihedral angle between the C-H_X and the C-NO_2 bonds is found to be 90° with the nitro group oriented away from the phthalan part of the molecule. It is of special interest to determine whether the same conformation is also favored in solution and to this end we have analyzed the proton magnetic resonance spectra of I in $CDCl_3$.



I



Orientation of the nitro group in the crystal of trans-1-(nitromethyl)-3-phenylphthalan.

The ABXY patterns (Figures 1 and 2) afforded by the proton spectra of both the cis and trans isomers were analyzed with the aid of LAOCOON III (3,4). The results are tabulated in Table I.

The dihedral angles of the C-H_A and C-H_B bonds with respect to the C-H_X bond were calculated from the observed couplings, J_{AX} and J_{BX}. The standard Karplus equation as derived for an unsubstituted ethanic fragment (5) was chosen for this purpose on the basis of the following consideration. First, the large number of strongly electronegative groups attached to the two carbons of interest is expected to reduce the value of J_{vic} by several Hz relative to ethane (6). However, the oxygen atom in the five-membered heterocyclic ring with unshared electrons in the *p*-orbitals coplanar with the adjacent C-H_X bond is expected to enhance the value of J_{vic} by as much as +2.3 Hz (7). Thus, to a first approximation, these two opposing factors operating on J_{vic} will more or less cancel one another.

The average orientation of the C-H_X and C-NO_2 bonds is calculated to be about 85° for I and 75° for II. These values are believed to be reasonably accurate because H_A and H_B are oriented such that their dihedral angles fall on the $\cos^2\theta$ function where J is most rapidly changing with angle θ, and which is roughly linear. The linearity explains why the sum of J_{AX} and J_{BX} is constant, 11.6 ± 0.1 Hz for I and II. The sensitivity of the coupling to the angle may be judged by the fact that if the C-H_X-C-NO_2 dihedral angle is changed from 80° to 90°, the corresponding couplings are changed by *ca.* 1.6 Hz.

That the average orientation of the C-H_X and C-NO_2 bonds for solutions of I in $CDCl_3$ is about 85°, and within experimental error the same as in the crystal, is very interesting and, of course, what one would hope would be the general situation for X-ray analysis of conformations. Obviously, in many cases this is not true, as illustrated by the examples of biphenyl, which is planar in the crystal (8), and chlorocyclohexane, which crystallizes as the equatorial isomer (9).

TABLE I

LAOCOON III NMR Spectral Parameters of cis- and trans-1-(Nitromethyl)-3-phenylphthalan in $CDCl_3$ at 60 MHz[a]

Parameter	I trans[b]	II cis	Parameter	I trans[b]	II cis
δ_A	278.2	281.5	J_{AY}	-0.1	-0.1
δ_B	281.4	287.1	J_{BX}	6.3	3.4
δ_X	364.9	357.2	J_{BY}	-0.3	0.0
δ_Y	376.8	370.9	J_{XY}	±2.9	±2.1
J_{AB}	-12.7	-12.9	RMS Error	0.09	0.06
J_{AX}	5.4	8.2			

[a] Freshly prepared solutions (4). Chemical shifts in Hz relative to TMS, and all couplings in Hz. [b] These parameters also fit the 220-MHz spectra of the trans isomer.

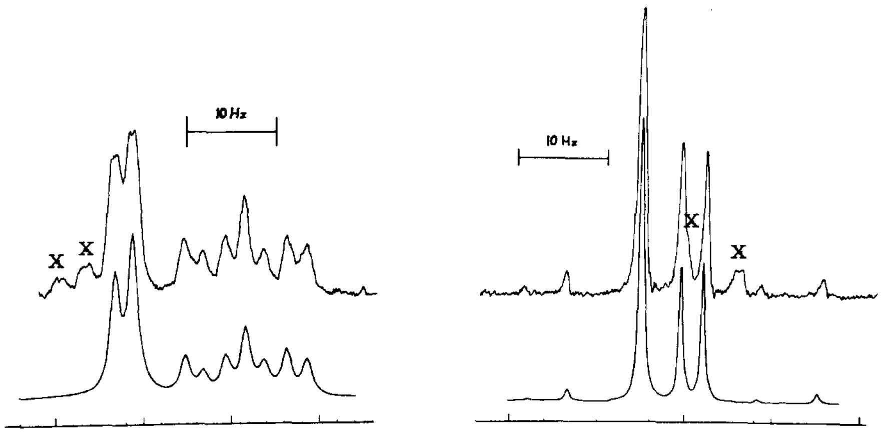


Figure 1. Pmr spectra at 60 MHz, observed and calculated for cis-1-(nitromethyl)-3-phenylphthalan in $CDCl_3$. Peaks marked (X) correspond to small amounts of the trans isomer.

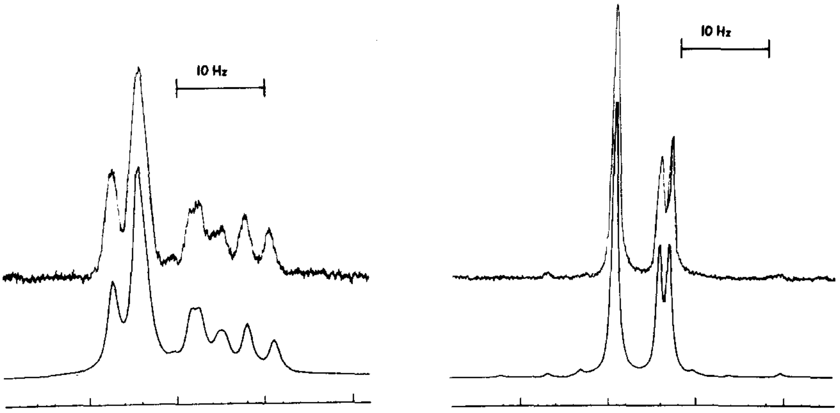


Figure 2. Pmr spectra at 60 MHz, observed and calculated for trans-1-(nitromethyl)-3-phenylphthalan in $CDCl_3$.

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1. (a) The work carried on at the California Institute of Technology was supported by the National Science Foundation. (b) Contribution No.

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4. The trans isomer decomposes slowly in $CDCl_3$ with the ultimate separation of an aqueous phase. Presumably this is the result of an acid-catalized ether-ring opening followed by dehydration. This decomposition causes marked changes in J_{AX} (increased by 2.8 Hz), J_{BX} (decreased by 3.2 Hz), and $\Delta\nu_{AB}$ (increased by 2.7 Hz).

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