methyl oleate). The gas chromatogram on a 10% butanediol succinate column on Chromosorb W at 175° showed 63% methyl oleate.

Vinyl Chloride Hydrogenation. A 1.0% solution of $PtCl_2$ in a mixture of 44 g of $[(n\text{-}C_4H_9)_4N][SnCl_3]$ and 17 g of $[(C_2H_5)_4N][SnCl_3]$ was melted, evacuated, and cooled to 25°. The glass reactor was pressured to 25 psig with vinyl chloride and was reheated to 70°. Some vinyl chloride dissolved but no reaction occurred over 3 hr. The reactor was heated to 120° and the gas was replaced with an equimolar mixture of hydrogen and vinyl chloride. A rapid pressure drop occurred. Gas chromatographic analysis showed only ethane and vinyl chloride.

In a subsequent experiment, an equimolar mixture of H_2 and vinyl chloride was heated at 105° for 3 hr with a 1% solution of $PtCl_2$ in Et_4NSnCl_3. The conversion level (*ca.* 20%) was lower than in the earlier experiment, but even at this stage the predominant product was ethane. A small amount of ethylene also appeared.

Ethylene Hydroformylation. A solution of 0.6 g of platinum dichloride and 51 g of tetraethylammonium trichlorostannate was placed in a glass-lined 400-ml Hastelloy pressure vessel. The vessel was pressured to 1000 atm with a 1:2:10 mixture of hydrogen, ethylene, and carbon monoxide and was agitated at 90° for 6 hr. The volatile products were fractionated by vacuum distillation. The product retained by a trap cooled to −119° was propionaldehyde. Treatment with 2,4-dinitrophenylhydrazine gave a yellow-orange product. Recrystallization from ethanol gave orange needles of the 2,4-dinitrophenylhydrazone of propionaldehyde, melting point 154–156°. A mixture melting point with an authentic sample was not depressed. Vacuum distillation of the residual liquid clinging to the frozen salt in the pressure vessel gave 2.8 g of clear colorless liquid. Gas chromatographic analysis showed the presence of propionaldehyde and 2-methyl-2-pentenal.

Carbomethoxylation of Hexene. A mixture of 45 g of 1% $PtCl_2$ in $[(C_2H_5)_4N][SnCl_3]$ solution, 8.4 g of 1-hexene, and 4.8 g of methanol was heated at 90° for 6 hr under 450 atm CO pressure in a 400-ml glass-lined shaker tube. Gas chromatography of the crude supernatant liquid showed methyl heptanoate and methyl 2-methylhexanoate in a ratio of 4.1:1.

Nuclear Magnetic Resonance Spectra of 1:1 Adducts of 1,10-Phenanthroline and α,α′-Bipyridyl with Tris[2,2,6,6-tetramethylheptane-3,5-dionato] Complexes of the Lanthanides[1,2]

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Contribution from Coates Chemical Laboratory, Louisiana State University, Baton Rouge, Louisiana 70803. *Received March 21, 1972*

Abstract: The pmr spectra of solutions of 1:1 adducts of dpm_3 complexes of Eu, Pr, and Yb with 1,10-phenanthroline (phen) and α,α′-bipyridyl (bipy) have been studied. The pseudocontact shifts recorded for these complexes do not accord with the Robertson–McConnell expression, which assumes axial symmetry about the metal–Lewis base atom bond. Whereas the spectra of the phen complexes are rather insensitive to variations in temperature, a conformational process involving biphenyl-type rotational isomerization is deduced from the temperature dependence of $Eu(dpm)_3 \cdot$bipy. These complexes do not coordinate efficiently with added substances and are, therefore, of no value as shift reagents.

In the mere 3 years following the illustration by Hinckley[4] of the effect of tris(diketonato)europium (III) complexes upon the chemical shifts of protons in the vicinity of Lewis basic centers, literally hundreds of reports[5] have appeared describing facets of the interaction between a variety of lanthanide complexes and supernumerary substrates and of the influences thus wrought upon the field position of proximal, resonating nuclei in these substrates. The examples employed in studies of the shift-inducing properties[6] have in common the feature that all behave as monodentate ligands in their coordination to the metal, even though some are in fact multifunctional[7,8] and exhibit (mono) coordination at more than one functional group. In such lanthanide–Lewis base complexes it was found that the magnetic susceptibility tensor of the paramagnetic feature exhibits apparent $C_{\infty v}$ symmetry about the metal atom–Lewis basic atom bond, and that induced shifts (ΔH_i) can be calculated from the relationship[9]

$$\frac{\Delta H_i}{H_0} = \frac{k(g)(3\cos^2\theta_i - 1)}{r_i^3}$$

in which H_0 is the static field, θ_i is the angle about the metal ion between the bond defining the $C_{\infty v}$ axis and the ith nucleus, r_i is the distance of the ith nucleus from the electron cloud around the metal ion, and $k(g)$ is an empirically determined (generally) value that reflects the relative size of the components of the susceptibility tensor along ($g_{\parallel}$) and normal to ($g_{\perp}$) the $C_{\infty v}$ axis.[5,9] Numerous successful applications[5] have shown that the dependence upon θ_i can be overlooked in most cases without altering drastically the calculated shifts, although a few examples have been reported for which the errors introduced by this neglect are astronomical.[10]

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[1] This research was supported, in part, by Grant No. GP-4938 from the National Science Foundation (to J. Selbin).

[2] For the preceding paper, see N. Ahmad, N. S. Bhacca, J. Selbin, and J. D. Wander, *J. Amer. Chem. Soc.*, **93**, 2564 (1971).

[3] Author to whom correspondence should be addressed.

[4] C. C. Hinckley, *ibid.*, **91**, 5760 (1969).

[5] For a moderately selective review, see W. D. Horrocks, Jr., and J. P. Sipe, III, *ibid.*, **93**, 6800 (1971).

[6] J. K. M. Sanders and D. H. Williams, *ibid.*, **93**, 641 (1971).

[7] C. C. Hinckley, M. R. Klotz, and F. Patil, *ibid.*, **93**, 2417 (1971).

[8] N. H. Fischer, R. Wiley, and J. D. Wander, *Chem. Commun.*, 137 (1972).

[9] H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958); D. R. Eaton and W. D. Philips, *Advan. Magn. Resonance*, 1, 103 (1965).

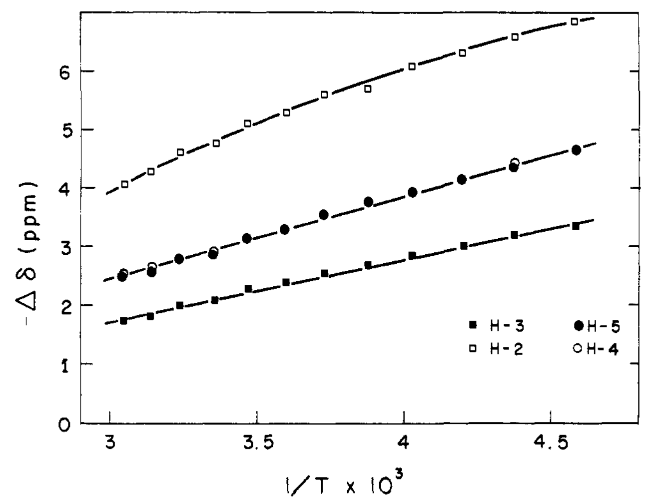


Figure 1. Induced shifts of proton resonances in Eu(dpm)$_3$·phen (1) as a function of temperature. No singularities are in evidence.

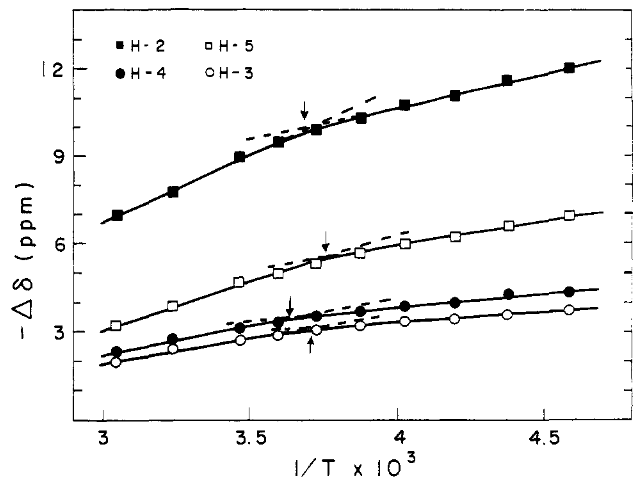
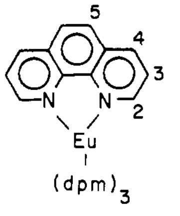


Figure 2. Induced shifts of proton resonance in Eu(dpm)$_3$·bipy (2) as a function of temperature; the region of greatest change of slope is marked and indicates the conformational process illustrated in Figure 5.

Results and Discussion

Inapplicability of the Robertson–McConnell Relationship. It was found impossible to apply the logical framework constructed above to rationalize the observed shifts of the aromatic proton resonances (numbered according to the illustrated convention) of 1:1 complexes[11] of Ln(dpm)$_3$[12] with the bidentate



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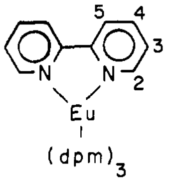

2

ligands 1,10-phenanthroline (phen) and α,α'-bipyridyl (bipy). Precise values of r_i and θ_i were computed[13] for Ln(dpm)$_3$·phen assuming Ln–N bond distances ($r_{\text{Ln-N}}$) in the range of values from 2.4 to 4.0 Å and other interatomic distances and bond angles to be equal to those determined for ZnCl$_2$·phen.[14] Similar computations were performed for the bipy analogs in which $r_{\text{Ln-N}}$ and the dihedral angle (ϕ) between the two aromatic rings were varied simultaneously over the ranges 2.4–4.0 Å and 0–30°, respectively, and the remaining bond parameters were those employed by McKenzie.[15]

Bidentate coordination for all the complexes in this study was assumed by analogy to the solid state structures and supported by the sluggish exchange processes[16] (see below) with added bipy or phen. Values of $\Delta H_i/H_0$ were calculated from these computed parameters according to two assumptions. Firstly it was assumed that the susceptibility tensor was cylindrically symmetrical with the axis bisecting the aromatic ligand; in the second instance the improbable assumption was made that each Eu–N bond defines a $C_{\infty v}$ axis, and net shifts were calculated that would account for such a dual interaction. In both cases the aromatic protons α and β to the heteroatom are predicted to shift in opposite directions, in disagreement with the observed, uniformly directed displacements. A similar calculation made by considering only one Eu–N bond predicted shifts at even greater variance. One may attempt to rationalize the observed behavior as indicative of a system that has either (a) an unsymmetrical susceptibility tensor, (b) considerable delocalization of unpaired electron density into the aromatic ligand, or, more likely, (c) both.

Temperature-Dependent Effects. Figure 1 depicts the temperature dependence of the chemical shifts measured for the proton resonances of Eu(dpm)$_3$·phen (1). Consistent with earlier observations,[3,16] the induced shift ($\Delta\delta$) is seen to increase monotonically with decreasing temperature. The corresponding plot (Figure 2) for Eu(dpm)$_3$·bipy (2) does not, however, show this regular behavior but rather exhibits at about room temperature ($T \sim 30°$) a change in the value of $d\Delta\delta/dT$ for all four of the aromatic proton resonances. Comparison of the line widths of representative signals from the spectra of 1 and 2 (Figure 3) as a function of temperature reveals that the H-2 and H-4 signals of 1 maintain approximately constant line widths until the temperature decrease causes the viscosity of the solutions to increase, whereas the signals of H-2 and H-5 of 2 exhibit a narrow region of rather abrupt broadening slightly above room temperature in addition to the predictable increase in line width near the lower temperature limits (Figure 4). Qualitatively similar observations were noted for the Yb analogs, although the line widths are so large that quantitation is impractical.

The line-broadening in the spectrum of 2 near room temperature is suggestive of an intermediate rate of

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[10] (a) N. S. Bhacca and J. D. Wander, *Chem. Commun.*, 1505 (1971); (b) B. L. Shapiro, J. L. Hlubucek, G. R. Sullivan, and L. F. Johnson, *J. Amer. Chem. Soc.*, **93**, 3281 (1971); (c) T. H. Siddall, III, *Chem. Commun.*, 452 (1971).

[11] J. Selbin, N. Ahmad, and N. S. Bhacca, *Inorg. Chem.*, **10**, 1383 (1971).

[12] Ln = Eu, Pr, Yb; dpm = 2,2,6,6-tetramethylheptane-3,5-dionato.

[13] These calculations were accomplished using a program COORDANG developed by Mr. Robert Duke of this department.

[14] C. W. Reimann, S. Block, and A. Pereoff, *Inorg. Chem.*, **5**, 1185 (1966).

[15] E. D. McKenzie, *Coord. Chem. Rev.*, **6**, 187 (1971).

[16] F. A. Hart, J. E. Newbery, and D. Shaw, *J. Inorg. Nucl. Chem.*, **32**, 3585 (1970).

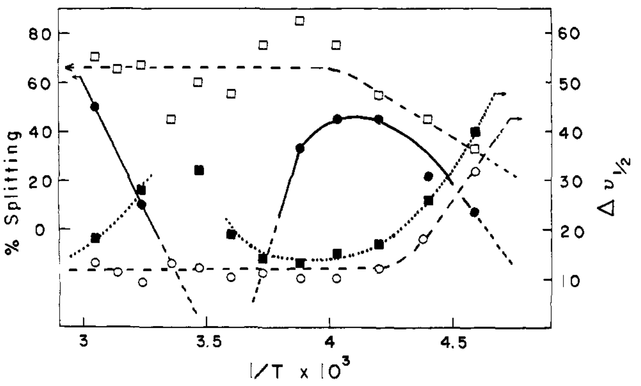

Figure 3. Variation of line width with temperature for the H-2 (○) and H-4 (□) signals of **1** and the H-2 (■) and H-5 (●) signals of **2**; the line widths of the H-2 signals are measured at half-height and refer to the right-side ordinate scale, wheras the extent of splitting of the well resolved H-4 (**1**) and H-5 (**2**) patterns represents an indirect measure of the width of these lines.

exchange between interconverting forms.[17] Bearing in mind that phen is a rigid, virtually planar system, whereas bipy possesses some rotational freedom about the C-6–C-6′ bond, one can at once postulate that above room temperature the two aromatic rings of bipy in **2** undergo a scissoring motion with respect to each other, which results in a rapid interconversion between two limiting conformers having local C_2 symmetry in the Eu·bipy portion (Figure 5). At lower temperatures, however, **2** exists as an equilibrium mixture of the two conformers, which are constrained to remain in one or the other conformation owing to the lowered average free energy. This is consistent with the observation that the pmr spectrum of **2** exhibits substantially the same pattern shapes (but at different shifts) and coupling constants above and below the presumed transition temperature, and provides an amusing example of molecular futility.

An additional feature that one observes on cooling the solutions of **2** in deuteriochloroform is that below the transition temperature the H-2 resonance is broadened and the coupling interactions to this nucleus have disappeared from the spectrum owing to paramagnetically enhanced relaxation of this nucleus. In the spectra of **3** and **4**, the H-2 signal is not observed at all (presumably due to the same effect) and no splittings that would arise from this nucleus are observed (Table I).

Interactions with Added Coordinating Agents. Hart, Newbery, and Shaw[16] examined the exchange between bound and free bipyridyl-derived ligands (L) in solutions of $Eu(NO_3)_3L_2$ and found that the exchange rate is temperature dependent. An analogous exchange occurs in solutions containing **1** or **2** and an excess of phen or bipy, respectively; no change in signal line width or position is observed, however, on addition of excess $Eu(dpm)_3$ to **1** or **2**. This is consistent with the mechanism of exchange (expanded coordination to accommodate an extra ligand and subsequent expulsion of one) proposed by Hart, *et al.*[16]

The initial report on shift reagents employed $Eu(dpm)_3$ as a pyridine adduct, which was found to dissociate in order to accommodate added Lewis bases.

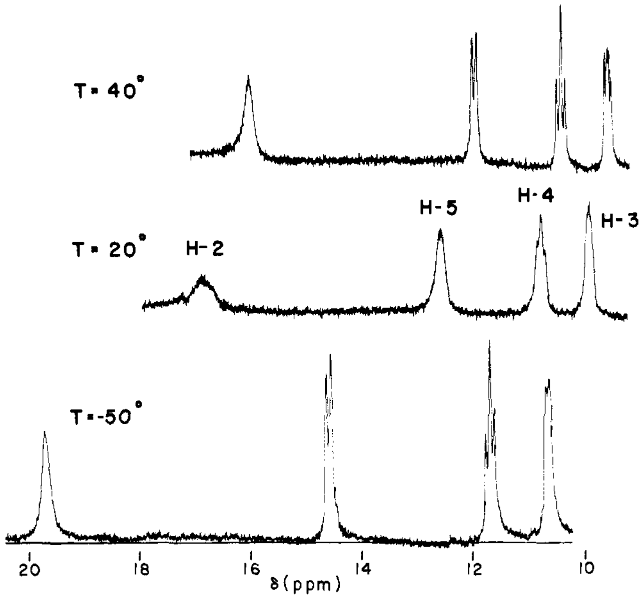

Figure 4. The 100-MHz nmr spectra of **2** at several temperatures; chemical shifts are expressed in ppm downfield from Me_4Si.

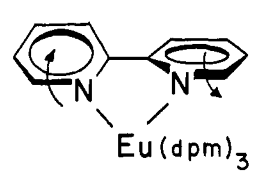

Figure 5. Motion of **2** to invert chirality of the local C_2 axis.

Table I. Nmr Spectral Parameters (100 MHz, 35°) for Aromatic Resonances in phen and bipy Monoadducts of $Ln(dpm)_3$

			Chemical Shifts[a]			
	Ln	L	H-2	H-3	H-4	H-5
1	Eu[b]	phen	14.14	9.92	11.34	10.87
3	Yb[c]	phen	*d*	22.34	15.93	23.82
4	Pr[c]	phen	*d*	−2.78	0.90	2.03
2	Eu[b]	bipy	16.44	9.62	10.50	12.27
			Coupling Constants, Hz			
			$J_{2,3}$	$J_{2,4}$	$J_{3,4}$	$J_{4,5}$
1	Eu[b]	phen	4.3	1.4	8.1	
3	Yb[c]	phen	*e*	*e*	3	
4	Pr[c]	phen	*e*	*e*	~3	
2	Eu[b]	bipy	4		7	7

[a] In ppm downfield from Me_4Si. [b] In chloroform-*d*. [c] In carbon tetrachloride. [d] Not observed. [e] Decoupled from the spectrum so not observed.

The original intent of this study was to examine **1**, **2**, and the Yb and Pr analogs as potential shift reagents. The addition of small amounts of ethanol to solutions of **1** or **2** in carbon tetrachloride, however, resulted in no change in the resonances (even of the hydroxyl proton) of the alcohol. The same experiment using $Yb(pdm)_3$·bipy (3 molar equiv) resulted in a slight downfield shift of the entire alcohol spectrum (due to the change in the bulk magnetic susceptibility of the solution) but essentially no alteration in the relative shifts. In a final test it was found that the spectra of **1** obtained in carbon tetrachloride and in acetone-d_6 are practically superimposable. It is thus apparent that the entropic gain from bidentate coordination to nitrogen

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[17] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonances," McGraw-Hill, New York, N. Y., 1959, pp 218–224.

atoms outweighs the higher intrinsic affinity of Ln for single oxygen atoms, and that these complexes are totally inapplicable as shift reagents.

Experimental Section

The preparation of compounds used in this study is described elsewhere.[11] Nmr spectra were recorded in frequency sweep or HR mode on a Varian HA-100 spectrometer fitted with a V-6040 variable temperature attachment, and are referenced to internal Me_4Si. Sample solutions were prepared either in carbon tetrachloride that had been stored over solid sodium hydroxide pellets or in commercial chloroform-*d*; each sample contained ~30 mg of complex per 0.3 cm^3.

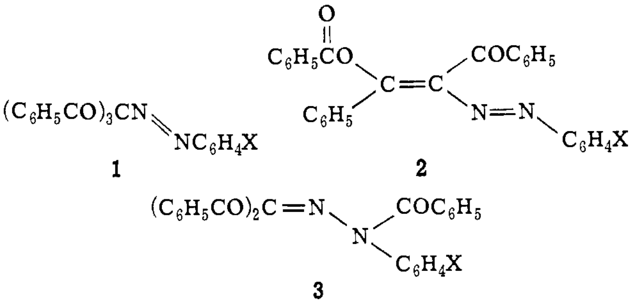
X-Ray Crystal Structure and Solid State Rearrangement of Phenylazotribenzoylmethane and the X-Ray Crystal Structure of α-*p*-Bromophenylazo-β-benzoyloxybenzalacetophenone[1,2]

Daniel B. Pendergrass, Jr., David Y. Curtin,* and Iain C. Paul*[3]

Contribution from the Department of Chemistry and the Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801. *Received February 2, 1972*

Abstract: The crystal structure of the unsolvated form of phenylazotribenzoylmethane (**1a**), a molecule which undergoes a solid state rearrangement to α-phenylazo-β-benzoyloxybenzalacetophenone (**2a**) and to diphenyl triketone *sym*-benzoylphenylhydrazone (**3a**), has been determined by X-ray analysis. The yellow crystals of **1a** are monoclinic with a = 13.054 (5), b = 10.352 (5), c = 16.560 (10) Å; and β = 90.78 (1)°. The space group is $P2_1/c$ and there are four molecules of **1a** in the unit cell. The structure has been refined to an R factor of 0.047 on 2309 structure amplitudes measured on a diffractometer (Cu Kα radiation). While the crystal structure of **1a** is quite different from that of *p*-bromophenylazotribenzoylmethane (**1b**), the molecular conformations are almost identical and appear to be influenced by intramolecular C=O---C=O (carbonyl) interactions. Features of the molecular conformation of **1a** are two C(carbonyl)---O(carbonyl) distances of 2.667 (4) and 2.758 (4) Å and two C(carbonyl)---N distances of 2.698 (4) and 2.998 (5) Å. Similar relative orientations of carbonyl groups are found in other di- (and poly-) ketones. There are no intermolecular distances in **1a** involving migrating centers less than 4.79 Å. The crystal structure of α-*p*-bromophenylazo-β-benzoyloxybenzalacetophenone (**2b**), one of the rearrangement products of **1b**, has also been determined. The red crystals of **2b** are triclinic, with a = 10.031 (3), b = 6.309 (3), c = 19.387 (6) Å; α = 96.78 (3), β = 103.78 (2), and γ = 90.54 (3)°. There are two molecules in the unit cell and the space group is $P\bar{1}$. The structure has been refined to an R factor of 0.099 on 3510 nonzero structure amplitudes measured on a diffractometer (Cu Kα). The stereochemistry about the N=N double bond is trans, while the migrating carbonyl group (to form **3b**) and the receiving *p*-bromophenylazo group are trans with respect to the C=C double bond. Kinetic studies of the rearrangement in the solid state of **1a** to a mixture of **2a** and **3a** showed, in the temperature range of 65–90°, an induction period followed by a rather good first-order fit through most of the reaction. Ratios of products **2a**:**3a** were independent of the origin of the starting material and of the fraction reacted but rather dependent on the temperature. The solid state rearrangements were slower than solution reactions by a factor of about 10^2. Chemically induced dynamic nuclear polarization and esr studies suggest that the rearrangements may be more complicated than might be inferred from the first-order kinetics observed in solution and in the solid state.

Phenylazotribenzoylmethane (**1a**) and a number of structurally related compounds have been shown to rearrange in good yield to a mixture of enol benzoate **2a** and hydrazone **3a** in nonpolar solvents at temperatures of 55° or higher.[4] Such rearrangements have also been found to occur in the solid state;[5] the solid state rearrangement of **1b** has been studied in some detail and the X-ray crystal structure reported.[6] The unbrominated compound **1a** has been of particular interest because it forms a crystalline hemietherate **1c** which loses the ether on standing to give **1a** in a different physical state.[7] This paper reports the X-ray crystal structure and studies of the effect of the solid state on



1 **2** **3**

a, X = H

b, X = Br

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(1) Taken in part from the Ph.D. Thesis of D. B. Pendergrass, Jr., submitted to the University of Illinois, 1971.

(2) We are indebted to the National Science Foundation and to the Advanced Research Projects Agency of the Department of Defense (Contract HC 15-67-C-0221) for support of this work.

(3) Alfred P. Sloan Research Fellow, 1968–1970.

(4) (a) See D. Y. Curtin and M. L. Poutsma, *J. Amer. Chem. Soc.*, **84**, 4887, 4892 (1962), and earlier references cited therein; (b) D. Y. Curtin and L. L. Miller, *ibid.*, **89**, 637 (1967).

(5) D. Y. Curtin, S. R. Byrn, and D. B. Pendergrass, Jr., *J. Org. Chem.*, 34, 3345 (1969).

(6) R. T. Puckett, C. E. Pfluger, and D. Y. Curtin, *J. Amer. Chem. Soc.*, **88**, 4637 (1966).

(7) J. D. McCullough, Jr., D. Y. Curtin, L. L. Miller, I. C. Paul, and D. B. Pendergrass, Jr., *Mol. Cryst. Liquid Cryst.*, **11**, 407 (1970).