

Interactions between Molecules and Superconductors

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Abstract: It is shown that the superconducting transition temperature and critical current of thin vanadium films are increased when electron donors are deposited on the film surface and decreased when electron acceptors are deposited, the absolute magnitude of the change being $\sim 0.1^\circ\text{K}$ in both cases. Preliminary work with indium films indicates that acceptors decrease the transition temperature and critical current, but that donors do not increase them.

The electronic and vibronic interactions thought to be responsible for superconductivity in metals are also present in molecules; but most molecules or molecular aggregates are not even potentially superconducting since they do not have a sufficiently high density of states near the Fermi energy. Even so, it has occurred to us that molecules can be coupled with a superconducting metal through various kinds of bonds, and that such systems may then have interesting superconducting properties. One approach to the preparation of such systems involves the deposition of selected molecules on thin metal films.

In a preliminary paper¹ we reported that depositing an organic molecule, 3,4,7,8-tetramethyl-9,10-phenanthroline (TMP), on a thin vanadium film raises its superconducting transition temperature by $\sim 0.09^\circ\text{K}$. We have now carried out a series of experiments, primarily with planar aromatic organic compounds, and have found more compounds which increase the transition temperature of vanadium films as well as others which decrease it. The sign of the effect can be correlated in a simple way with the electronic properties of these molecules. Compounds with low electronegativity increase T_c , while those with high electronegativity decrease it. The nature of these effects is partially clarified by comparison with similar experiments on indium films.

Experimental Procedure

As in our previous work, both metal and organic films were vacuum evaporated from resistance-heated sources through a fixed, helium temperature mask onto a single-crystal quartz substrate. The $1/8$ -in. thick substrate was in direct contact with liquid helium below its λ point. Pressures were less than 3×10^{-8} torr during the vanadium evaporations, less than 3×10^{-9} torr during the indium and organic evaporations, and were generally less than 6×10^{-10} torr at all other times. The mask was cut in the "H" geometry recommended by Newhouse.² That portion of the film whose critical current was measured was 0.006 in. wide (unless otherwise indicated) and 0.250 in. long. Contacts were usually made with air-dried, vacuum-baked, silver paint. The use of preevaporated, superconducting lead contacts produced no significant differences. To eliminate heat leaks the current and voltage leads were brought into the vacuum through the liquid helium. The voltage developed across the film was directly displayed as a function of current on a Moseley x-y recorder.

Metal was evaporated until the film was superconducting. The critical current, I_c , was then measured as a function of temperature over some limited range below the λ point. The critical current at a

particular temperature is defined here as that current necessary to restore a certain fixed resistance to the film,³ generally between 10^{-3} and 10^{-2} ohm. The critical current at a particular temperature did not change with time at a system pressure of 6×10^{-10} torr, but, to ensure that the surface remained uncontaminated by residual gases, the measurements were taken within 15 min of the film deposition.

The portion of the film being studied was then completely covered with an evaporated layer of the selected compound. This produced a change, often dramatic, in the critical current, which was monitored during the evaporation. The new I_c vs. T curve was then measured. Over the small temperature range studied, the new curve is identical in shape with that of the clean film but is displaced along the temperature axis. This displacement is assumed to equal ΔT_c , the change in the superconducting transition temperature produced by the compound. Both the sign and the magnitude of ΔT_c are insensitive to the exact definition of I_c (see Figure 1). In one experiment (no. 3, Table I; see Figure 2) the validity of the assumption about ΔT_c was tested by actually measuring T_c both before and after the chemical deposition. In Figure 2 the lateral displacement of the two curves varies between $+0.06$ and $+0.08^\circ\text{K}$ as the critical current changes by more than three orders of magnitude. This displacement agrees with the measured change in T_c of $+0.076^\circ\text{K}$. The differential nature of the experiment allows changes in T_c as small as 0.025°K to be measured easily.

Vanadium used for film no. 5 was nominally 99.8% pure. Spectroscopic analysis revealed the following impurities (in ppm): Cu, 1; Cr, 47; Fe, 344; Mg, 25; Mn, 178; Si, 1400. All other vanadium experiments were done with zone-refined, nominally 99.999% pure vanadium from Research Inorganic Chemicals. Spectroscopic analysis revealed no impurities. Film properties for the two purities are essentially the same. Vanadium films deposited at $\sim 2^\circ\text{K}$ are quench-condensed in a high resistivity, presumably highly disordered or even amorphous form, which exhibits a T_c considerably below 5.3°K , that of bulk vanadium.⁴ These films can be annealed. After the liquid helium is exhausted, the temperature rises slowly. Annealing begins at approximately 35°K , and the resistance decreases until 75°K . After $\sim 75^\circ\text{K}$ films show a positive temperature coefficient of resistance. The films can also be annealed by resistance heating with helium still present. Upon annealing, transition temperatures rose; normal film resistances dropped by factors of as much as 15 to 20. For unannealed films approximately 100 Å thick, transition temperatures were generally between 2.2 and 2.6°K , with an upward trend in T_c with increasing film thickness for both annealed and unannealed films. The critical temperature of some of the thicker annealed films was greater than 4.2°K . Little⁵ has observed transition temperatures of 3.95 – 4.68°K for annealed vanadium films 170–1000 Å thick, the thicker films having generally higher T_c . van Beelen, *et al.*,⁶ have seen transition temperatures from 1.8 to 4.6°K for thicknesses between 130 and 800 Å.

(3) The importance of this procedure is stressed by both (a) R. E. Glover, III, and H. T. Coffey, *Rev. Mod. Phys.*, **36**, 299 (1964); (b) A. P. Smirnov, U. N. Totubalin, and I. S. Parshina, *Soviet Phys. JETP*, **22**, 84 (1966).

(4) J. C. Suits, *Phys. Rev.*, **131**, 588 (1963).

(5) L. Meyers and W. A. Little, *Phys. Rev. Letters*, **13**, 325 (1964).

(6) H. van Beelen, *et al.*, "Eighth International Conference on Low Temperature Physics," R. O. Davies, Ed., Butterworth, Inc., Washington, D. C., 1962, p 378.

(1) H. M. McConnell, B. M. Hoffman, D. D. Thomas, and F. R. Gamble, *Proc. Natl. Acad. Sci. U. S. A.*, **54**, 371 (1965).

(2) J. W. Bremer and V. L. Newhouse, *Phys. Rev.*, **116**, 309 (1959); see also V. L. Newhouse, "Applied Superconductivity," John Wiley and Sons, Inc., New York, N. Y., 1964, Chapter IV.

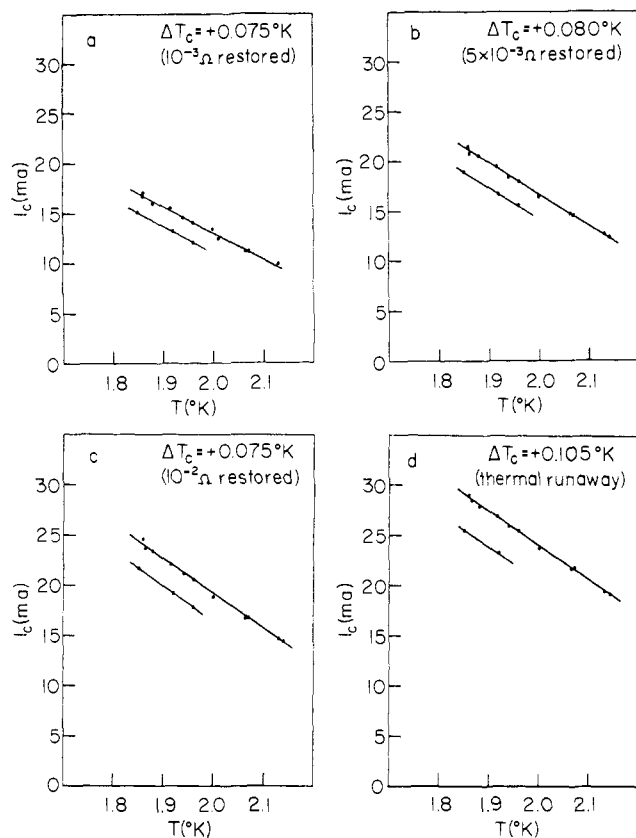


Figure 1. The critical current of a vanadium film plotted as a function of temperature before and after the deposition of tetracene for four different definitions of the critical current, I_c . The "before" curve is the lower one in each case (expt 2).

Our film thicknesses were usually estimated from the room temperature resistance $R(300^\circ\text{K})$, using a bulk resistivity, $\rho_B = 25 \times 10^{-6}$ ohm cm.⁷ The use of ρ_B is consistent with the data for Little's films which have an average room-temperature resistivity of 21.2×10^{-6} ohm cm. In addition, some high-resistivity films could apparently be nearly fully annealed at 4°K by resistance heating. This is indicated by a large decrease from the unannealed low-temperature resistance, $R(U)$, to the annealed, residual resistance, $R(A)$, and by the large resistance ratio $R(300^\circ\text{K})/R(A)$ (particularly films no. 8 and 12 but also no. 6). In these cases the thicknesses determined using the differences $R(300^\circ\text{K}) - R(A)$ and the temperature-dependent resistivity $\rho = 18.5 \times 10^{-6}$ ohm cm of van Beelen, *et al.*,⁸ are in excellent agreement with those determined from $R(300^\circ\text{K})$ and ρ_B .

From these and other vanadium films a linear relationship between $R(U)$ and $R(300^\circ\text{K})$ can be established: $R(300^\circ\text{K}) = 0.196 R(U) + 0.153$ kohm. The constants are obtained by the method of least squares, and the standard error of estimate is 0.053 kohm. This is used with measured values of $R(U)$ to approximate $R(300^\circ\text{K})$, and from this the thickness for those films for which $R(300^\circ\text{K})$ could not be measured.

The indium experiments were done with nominally 99.999% pure metal. Spectroscopic analysis revealed less than 5 ppm copper. Indium films evaporated onto a 4°K quartz surface were superconducting up to 4.1°K , as expected for quench-condensed indium films.⁸ The normal resistance of these films was reduced by a factor less than 4 on annealing.

The organic compounds used were either zone refined (anthracene) or recrystallized and then sublimed, usually two or more times. Paramagnetic impurities were not always removed by this procedure. They were sometimes found in very low concentration, but in both "enhancers" ($\Delta T_c > 0$) and "depressors" ($\Delta T_c < 0$).

(7) Taken from A. Morette, "Nouveau Traite de Chimie Minerale," Vol. XII, P. Pascal, Ed., Masson et Cie., Paris, 1958, p 37.

(8) J. M. Blatt, "Theory of Superconductivity," Academic Press Inc., New York, N. Y., 1964, p 361.

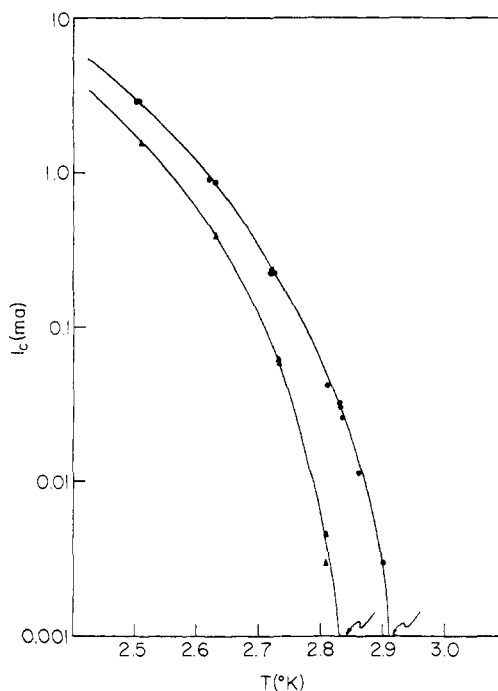


Figure 2. The critical current of a vanadium film plotted as a function of temperature before and after the deposition of perylene (\blacktriangle , before; \bullet , after). Arrows indicate the transition temperatures (expt 3).

Temperatures were determined from the vapor pressure of the pumped helium. The pressures were measured with a precision manometer via a tube which terminated near the substrate. Except for the actual measurement of T_c , experiments were routinely done entirely below the λ point in order to eliminate thermal gradients in the liquid helium. These precautions were taken to ensure that the temperature at the helium side of the quartz substrate should be very close to the temperature derived from the helium vapor pressure curve. Thermal gradients across the substrate caused by room temperature radiation should be quite small because of the high thermal conductivity of the quartz at these temperatures and because of the shielding provided by one liquid nitrogen and two liquid helium temperature heat shields. The effectiveness of this arrangement is demonstrated by the fact that films held at $\sim 2^\circ\text{K}$ (indicated), later shown to have transition temperatures only 0.2°K higher, were superconducting during the latter part of the metal evaporation, while hot metal atoms were striking the surface and with the source at approximately 2000°K 10 in. away.

Discussion of Results

Experimental results for the compounds studied are listed in Table I. It can be seen that most enhancers increase T_c by 0.05 to 0.10°K , and that depressors decrease T_c by 0.05 to 0.11°K for films with transition temperatures between 2.2 and 2.6°K .⁹ The variability in film properties between experiments makes the variations in magnitude of ΔT_c within each group of perhaps secondary significance.

As mentioned above, the sign of ΔT_c for the compounds studied can be related to a division of the molecules according to electronegativity, ψ . We use Mulliken's definition, $\psi = \frac{1}{2}(I + A)$ where I is the first ionization potential and A the electron affinity.¹⁰ Where available, I and A are given in Table I, columns 10 and 11. For most of these compounds, they are not both

(9) It was also possible to prepare vanadium films in a low-resistivity, annealed form prior to organic deposition. Experiments with these annealed films give similar enhancements to those with unannealed films (expt 5, Table I).

(10) R. S. Mulliken, *J. Chem. Phys.*, 2, 782 (1934); 3, 573 (1935).

Table I

Expt	Compound	ΔT_c , °K	T_c , °K	Film width, ^b mm $\times 10$	$R(U)$, kohm	$R(A)$, kohms	$R(300)$, kohms	—Thickness,— A, from		I , ev	A , ^t ev	ψ , ev	
								R (300)	$R(300)$ — $R(A)$				
Vanadium Films													
1	Anthracene	+0.10	2.33	2.54	2.80	(0.400) ^e	0.70	1.75	89		7.23 ^g	0.42	3.83
2	Tetracene	+0.075	2.76	2.54	1.70				128 ^f		6.88 ^g	1.0	3.94
3	Perylene	+0.08	2.92	1.52	2.48	0.22	0.51	2.32	204	265	7.15 ^g	0.85	4.0
4	Phenothiazine	+0.09	2.2	1.52	6.80	(1.01) ^e	1.63	1.62	64		7.28 ^h		
5	3,4,7,8-Tetramethyl- 1,10-phenanthroline	+0.09	2.45	2.54 ^c	3.02				84 ^f		8.65 ⁱ		
6	2-Aminoanthra- quinone	+0.06	2.62	1.52	3.80	0.285	0.900	3.16	116	125	$\lesssim 9.34$ ^j	< 0.5 ⁱ	$\lesssim 4.9$
7	1,4,5,8-Tetrachloro- anthraquinone	+0.025	2.23	1.52	9.25				50 ^f		$\gtrsim 9.34$ ^j	0.66 ⁱ	$\gtrsim 5.0$
8	Pyromellitic dian- hydride	-0.11	2.25	1.52	6.33	0.445	1.56	3.5	67	69		0.85	
9	Chloranil	< 0 ^a		2.54 ^c							$\gtrsim 9.68$ ^k	1.37	$\gtrsim 5.5$
10	Tetracyanoquino- dimethan	-0.10	2.25	1.52	7.6	0.600	1.72	2.87	60	68		1.7	
11	Tripyridyl-s-triazine	+0.05	3.6 ^d	1.52	0.750 ^d	0.655	1.67	2.58	62	78			
12	Dicyclopentadienyl titanium dichloride	-0.05	2.42	2.54	3.63	0.222	0.780	3.5	80	83			
Indium Films													
13	3,4,7,8-Tetramethyl- 1,10-phenanthroline	0.00	4.1	1.52	6.3	4.58	11.7 ⁱ						
14	Tetracyanoquino- dimethan	-0.23	4.09	1.52	3.28	0.843	1.38 ⁱ						

^a Film was destroyed after the initial critical current depression was observed, but before ΔT_c could be measured. ^b All films, 6.35 mm long. ^c Newhouse geometry not used. ^d Vanadium was deposited in an essentially annealed form. Experiments with this compound on unannealed films were similar. ^e Not fully annealed. ^f Estimated from $R(U)$ as described in text. ^g From R. W. Kiser in "Introduction to Mass Spectrometry," Prentice-Hall Inc., Englewood Cliffs, N. J., 1966, Appendix IV. ^h From M. Kinoshita, *Bull. Chem. Soc. Japan*, **35**, 1609 (1962). ⁱ Estimated in this laboratory from charge-transfer absorption spectra. ^j Ionization potential of unsubstituted anthraquinone = 9.34. ^k Ionization potential of unsubstituted quinone = 9.68. ^l From G. Briegleb, *Angew. Chem. Intern. Ed. Engl.*, **3**, 617 (1964), except where noted.

known. However, if the molecules are divided into enhancers and depressors of T_c it is seen that all depressors act as acceptors in intermolecular charge-transfer complexes, while most of the enhancers are either well-known charge-transfer donors (anthracene, tetracene, perylene, phenothiazine)¹¹ or can function as such (TMP).¹² Acceptors characteristically have high ψ , and donors, low ψ . Therefore the division of these enhancers and depressors on the basis of electronegativity is immediate.

Also among the enhancers are the substituted anthraquinones. These were chosen because it was expected that as ψ was systematically decreased, the sign of ΔT_c would change at some point. They are weak charge-transfer acceptors whose electron-affinity values¹³ are less than those of tetracyanoquinodimethan (TCNQ), chloranil, and pyromellitic dianhydride (PMA). If we consider the electronegativities for the charge-transfer acceptors to parallel their known A values, then all the planar aromatic compounds studied can be arranged according to ψ and a division made which separates enhancers from depressors, this division coming between PMA and 1,4,5,8-tetrachloroanthraquinone.

(11) For recent reviews of intermolecular charge-transfer systems, see (a) R. S. Mulliken, *J. Chim. Phys.*, **60**, 20 (1963); (b) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962); (c) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

(12) Charge-transfer complexes of TMP with the acceptors tetracyanoethylene and 2,3-dichloro-5,6-dicyanobenzoquinone have been prepared in this laboratory. The derived value of I for TMP is listed in Table I.

(13) Table I, column 11.

The two additional chemicals studied, tripyridyl-s-triazine (TPTZ) and dicyclopentadienyltitanium dichloride (DCT), are not *planar* aromatics. They can, however, be reasonably arranged by electronegativity with the planar compounds, and the signs of ΔT_c correspond to the above division. The pyridine rings of TPTZ ($\Delta T_c = +0.05$) are sterically prevented from lying in the plane of the triazine ring, but the molecule should still be a weak electron donor with ψ between that of TMP and the anthraquinones; thus it should be possible to place it by electronegativity with the other enhancers. DCT ($\Delta T_c = -0.05^\circ\text{K}$) is readily reduced, indicating the ease of the reaction $\text{Ti}^{\text{IV}} + e^- \rightarrow \text{Ti}^{\text{III}}$ and the correspondingly high electronegativity of the molecule; it can therefore reasonably be placed with the other depressors.

The division by electronegativity does not, however, specify the detailed mechanism by which the changes in superconducting properties are produced. Static charging experiments on indium films by Glover and Sherrill¹⁴ indicate that electron withdrawal increases T_c ; however, depositing TCNQ, a very strong acceptor, on indium films gives $\Delta T_c = -0.23^\circ\text{K}$, the wrong sign for simple electron abstraction. Except in the case of oxygen, the bonds of molecules to transition metal surfaces, although polarized, are generally considered to be largely covalent and dependent on partially filled d orbitals as in the metallocene complexes of transition

(14) R. E. Glover, III, and M. D. Sherrill, *Phys. Rev. Letters*, **5**, 248 (1960); see also H. L. Stadler, *ibid.*, **14**, 979 (1965); W. Ruhl, "Ninth International Conference on Low Temperature Physics," T. G. Daunt, *et al.*, Ed., Plenum Press, New York, N. Y., 1965, p 475.

metals and organic molecules.¹⁵ The null effect of TMP on the nontransition metal indium ($\Delta T_c = 0$) may indicate that the enhancements seen on vanadium ($\Delta T_c = +0.09^\circ\text{K}$) are related to π -d bonding between the unfilled d orbitals of the metal and the π molecular orbitals of the molecule.¹⁶

(15) D. O. Hayward and B. M. Trapnell, "Chemisorption," Butterworth, Inc., Washington, D. C., 1964, Chapter VII.

(16) NOTE ADDED IN PROOF. In a private communication, R. E. Glover has kindly pointed out to us that electron withdrawal in *unannealed* indium thin films *decreases* the transition temperature. Further discussion of this point and additional experimental results are presented elsewhere (H. M. McConnell, F. R. Gamble, and B. M. Hoffman, *Proc. Natl. Acad. Sci. U. S.*, to be published).

Conclusion

We feel that the possibility of correlating molecular properties with molecular effects on superconductivity in what is yet a preliminary investigation of a new phenomenon augurs well for an eventual understanding of the microscopic mechanisms involved and for the profitable extension of these studies to other systems.

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Some Generalizations Concerning the Magnetic Circular Dichroism of Substituted Benzenes¹

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Abstract: The magnetic circular dichroism (MCD) of a series of substituted benzenes has been measured. It was found that there is a correlation between the magnitude and sign of the MCD and the substituent's Hammett σ_{para} value for both the mono- and disubstituted benzenes. The MCD also appears to be quite sensitive to the symmetry of the derivative being smaller in molecules with higher symmetry.

Recently the authors published a note² in which it was suggested that the magnetic circular dichroism (MCD) observed in aromatics originated in the magnetically induced mixing of their B_{1u} and B_{2u} states. The object of this communication is to: (1) extend the results presented earlier to a series of benzene derivatives; (2) point out some generalizations which can be made concerning these data; and (3) provide additional evidence for the mixing of the B_{1u} and B_{2u} states.

At this time the authors feel that there is little reason for publishing extensive MCD spectra. Instead, apart from Figure 1, the experimental results will be summarized by indicating whether the B_{2u} bands have a positive or negative³ MCD. Since the assignment of the B_{2u} band is not always certain, the approximate wavenumber (in kilokaisers) used is indicated in parentheses after the name of the compound.

Experimental Section

The MCD was measured on a JOUAN dichrograph with very extensive modifications which included (1) the use of a 500-w xenon arc light⁴ source; (2) the replacement of the original monochromator

with one of the type used in a Cary Model 15 spectrophotometer; (3) changing the crystal modulation to 82 cps; (4) addition of an electromagnet capable of providing fields up to 13.1 kgauss in a 5-mm gap. Unless otherwise specified, all of the measurements to be reported were made in ethanol at concentrations sufficient to give an absorbance of 1 or 2. The molar MCD is defined as the experimental MCD per 10 kgauss divided by the product of the molarity and path length (in cm) of the sample. All of the comparisons made in the text are among the maximum molar MCD values observed in the B_{2u} bands. (Theoretically it would be more desirable to use the MCD integrated over the band. However the B_{2u} band widths and shapes are similar in all of the compounds studied so the ratio of the maximum MCD to the integrated MCD will be approximately constant.) While the precision of the MCD measurements was generally good to a few per cent, the absolute values given in Figure 1 are probably not accurate to better than 10% since literature molar absorptivities were used in calculating the molar MCD values.

For convenience in discussing the results, the compounds will be divided into four major classes and several subdivisions. The first three classes will include mono-, di-, and polysubstituted benzenes having a well-characterized MCD. The fourth class will include miscellaneous compounds which have a very small or ambiguous MCD.

Class Ia. Positive MCD. N,N-Dimethylamino (40.0 kK), amino (35.8), hydroxy (37.1, in aqueous 0.1 N HCl), methoxy (37.3), methyl (38.5), ethyl (37.0), chloro (38.0), bromo (38.5), and iodo (38.9).

Class Ib. Negative MCD. Carboxy (36.5), carboxylate (37.4, in aqueous 0.1 N NaOH), carbonyl (35.4), cyano (36.9), sulfonic (38.7), sulfonamide (37.8), and sulfonyl chloride (37.4).

Class IIa. Positive MCD. *o*-Aminohydroxy (35.1), *m*-aminochloro (34.3), *m*-aminobromo (34.1), *m*-hydroxymethyl (36.3), *p*-hydroxymethyl (35.7), and *o*-, *p*-, and *m*-dimethyl (all *ca.* 37.0).

Class IIb. Negative MCD. *p*-Nitrocarbonyl (33.3).

(1) This work was supported under a grant from the U. S. Public Health Service, Contract No. GM-11043.

(2) J. G. Foss and M. E. McCarville, *J. Chem. Phys.*, **44**, 4350 (1966).

(3) Since the sign of the MCD will be of some importance in this discussion, it should be pointed out that the sign convention used here is in agreement with that used for conventional Faraday measurements. This leads, for example, to a positive MCD near 20 kK for an aqueous cobalt chloride solution. Unfortunately, some workers, e.g., P. N. Schatz, P. J. Stephens, and co-workers, have chosen to use the opposite convention; see, for example, P. J. Stephens, W. Suëtaak, and P. N. Schatz, *J. Chem. Phys.*, **44**, 4592 (1966).

(4) J. G. Foss, *Anal. Chem.*, **35**, 1329 (1963).