

comparison of the coordination tendencies of ligands V and VIII. This conclusion is also supported by other comparisons made in a preliminary phase of this investigation, when it was observed that many bidentate ligands which were known to form 6-membered chelate rings with other metals were not effective with Zr(IV).

All of the results of this investigation are compatible with a maximum coordination number of 8 for aqueous Zr(IV) complexes. Because of the small radius of the Zr(IV) ion, however, complexes and chelates involving a lower coordination number of the metal are also possibly formed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CLARK UNIVERSITY]

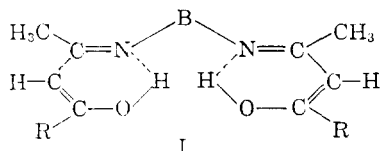
Dipole Moments of Metal Chelate Compounds. III. Analogs and Polar Substituted Analogs of Bis-acetylacetonediimine^{1,2}

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The electric dipole moments of some quadridentate Schiff base chelating agents have been determined and interpreted in terms of the polar groups present and of rotation of the hydrogen-bonded chelate rings about the alkylene bridge. Dipole moment values indicate that polar substituents such as *p*-bromophenyl, *m*-nitro and trifluoromethyl, occupy terminal positions in these molecules. In the benzoylacetonopolymethylenediimine series the dipole moments were found to increase with increasing number of methylene groups.

Earlier papers in this series³ have reported the results of dipole moment measurements on a series of quadridentate Schiff-base chelating agents and on the corresponding square planar chelates formed with transition metal ions. The present investigation describes similar studies of a number of closely related ligands. Its purpose was to observe the changes in dipole moment resulting from: (1) structural changes in the diimine portion of the Schiff base molecules and (2) the introduction of polar groups into the ligands. The compounds measured are given in Table I and may be represented by formula I in which B is the alkyl (or aryl) radical of the diamine and R represents various polar and non-polar groups.



Experimental

Procedure.—The syntheses and purification of the Schiff base ligands used in this investigation have been given previously.^{4,5} The method of measuring the dielectric constants and a description of the cell and heterodyne oscillator were reported in the first paper³ of this series. In all determinations benzene solutions of the ligands were employed. Because of their low solubilities many of the ligands containing polar groups required heating to obtain complete solution. All solutions employed had concentrations of 1% or less. Specific volumes were determined by means of a Rieschauer pycnometer. The cells used for the measurements were immersed in an oil-bath at 25°; for the determination of an individual dipole moment the temperature remained within $\pm 0.01^\circ$.

(1) Abstracted from a dissertation submitted by Richard J. Hovey to the Faculty of Clark University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1958.

(2) This work was supported by the Office of Ordnance Research under Contract No. DA-19-020-ORD-3243.

(3) P. J. McCarthy and A. E. Martell, *THIS JOURNAL*, **78**, 264, 2106 (1956).

(4) P. J. McCarthy, R. J. Hovey, K. Ueno and A. E. Martell, *ibid.*, **77**, 5820 (1955).

(5) R. J. Hovey, J. J. O'Connell and A. E. Martell, *ibid.*, **81**, 3189 (1959).

TABLE I

B	R	Name of ligand
CH(CH ₃)CH ₂	<i>p</i> -C ₆ H ₄ Br	Bis- <i>p</i> -bromobenzoylacetonetripropylenediimine
CH(CH ₃)CH ₂	CF ₃	Bis-trifluoroacetylacetonetripropylenediimine
(CH ₂) ₃	<i>m</i> -C ₆ H ₄ NO ₂	Bis- <i>m</i> -nitrobenzoylacetonetrimethylenediimine
(CH ₂) ₄	CH ₃	Bis-acetylacetonetetramethylenediimine
(CH ₂) ₄	C ₆ H ₅	Bis-benzoylacetonetetramethylenediimine
(CH ₂) ₅	C ₆ H ₅	Bis-benzoylacetonepentamethylenediimine
CH ₂ CH(OH)CH ₂	C ₆ H ₅	Bis-benzoylacetonediimino-2-propanol
<i>m</i> -C ₆ H ₄	CH ₃	Bis-acetylacetonediimino- <i>m</i> -phenylenediimine

Spectro-grade benzene, obtained from the Eastman Kodak Co., was refluxed over 40-mesh calcium hydride (Metal Hydrides, Inc., Beverly, Mass.) for approximately 48 hours, and then was distilled through a Widmer column, the first and last 15% being rejected. In comparison with the previous method of purifying benzene this new procedure is much simpler and far less time consuming. The dielectric constant of the solvent purified in this manner agreed with the earlier values within the desired limits.

Calculations.—The total molar polarization of the solute at infinite dilution ($P_{2\infty}$) was calculated by the method of Halverstadt and Kumler.⁶ $P_{2\infty}$ was obtained by means of the equation

$$P_{2\infty} = \frac{3\alpha v_1 M_2}{(\epsilon_1 + 2)^2} + M_2(v_1 + \beta) \frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)}$$

where α and ϵ_1 are the slope and intercept of the plot of ϵ_2 (the dielectric constant of a solution) against w_2 (the weight fraction), β and v_1 are the slope and intercept of the plot of v_{12} (the specific volume of a solution) against w_2 , and M_2 is the molecular weight of the solute. The least-squares method was used in evaluating the various slopes and intercepts.

The dipole moment μ is equal to $0.01281 (P_0 T)^{1/2}$, where T is the absolute temperature. The orientation polarization P_0 was obtained by subtracting P_E , the electronic polarization

(6) I. Halverstadt and W. Kumler, *ibid.*, **64**, 2988 (1942).

TABLE II
 DIPOLE MOMENTS AND RELATED PARAMETERS

Compound	ϵ_{12}	α	v_1	$-\beta$	P_E (cc.)	$P_{2\infty}$ (cc.)	$\mu(D.)$
Bis- <i>p</i> -bromobenzoylacetonepropylenediimine	2.2714	3.646	1.14690	0.4791	123.7	461.1	3.99
Bis-trifluoroacetylacetonepropylenediimine	2.2687	10.112	1.14655	.4058	67.9	737.3	5.70
Bis- <i>m</i> -nitrobenzoylacetone-trimethylenediimine	2.2714	11.891	1.14478	.3468	120.9	1120.9	6.96
Bis-acetylacetone-tetramethylenediimine	2.2736	6.870	1.14349	.2029	73.9	396.4	3.93
Bis-benzoylacetone-tetramethylenediimine	2.2732	4.589	1.14380	.2852	112.9	421.0	3.81
Bis-benzoylacetone-pentamethylenediimine	2.2726	5.362	1.14373	.2691	117.6	495.3	4.23
Bis-benzoylacetone-1,3-diimino-2-propanol	2.2733	3.879	1.14360	.2793	109.8	373.3	3.52
Bis-acetylacetone- <i>m</i> -phenylenediimine	2.2735	6.438	1.14435	.2535	79.5	402.0	3.93

tion, and P_A , the atom polarization, from $P_{2\infty}$. The methods of estimating P_E and P_A are the same as those described previously.³

Results

For each dipole moment determination dielectric constants (ϵ_{12}) and specific volumes (v_{12}) were measured for five or six solutions of varying concentration. Plots of these values against weight fraction (w_2) of the solute yielded straight lines in all cases. In Table II are listed the Halverstadt-Kumler parameters and dipole moment values of the eight ligands studied. As indicated in the earlier papers the dipole moment values are believed to be accurate to about $\pm 0.1 D$.

Discussion

For the bis-benzoylacetone-polymethylenediimine ligands having two to five carbon atoms between the nitrogen atoms, the observed increase of dipole moment is 3.21, 3.71, 3.81 and 4.23 D , respectively. Similar results have been observed in other polymethylene series, such as the polymethylene dibromides^{7,8} and dicyanides.⁹

Rotation around the carbon-carbon and carbon-nitrogen bonds makes it possible for the dipoles associated with the terminal groups to assume different positions relative to one another. However, all positions are not equally probable because of steric factors and the mutual repulsion of dipoles.

The large energy associated with the proximity of the end groups in the ethylenediimine Schiff base tends to keep the dipoles near a *trans*-configuration thus causing the moment of bis-benzoylacetoneethylenediimine to be considerably less than those of the compounds having longer polymethylene bridges. As the bridge length increases, there is a relative decrease in the potential energy for *cis* positions of the two end groups, so that their dipoles tend gradually to assume an average orientation in which all possible configurations contribute. While this explanation may account for the increase in dipole moment with increasing bridge length, by itself it does not satisfactorily account for the closeness in the moments of the trimethylene and tetramethylene derivatives. A similar situation occurs in the polymethylene dibromides, the dipole moments of which increase in the order 1.50, 1.97, 2.00 and 2.25 D , for two, three, four and five carbons between the bromine atoms, respectively.

According to the suggestion of Eyring,¹⁰ there is a van der Waals potential between the end groups, which gives rise to attraction, and tends to increase the molecular moment. Superimposed on this effect are the electrostatic forces between the dipoles, which affect the positions of the polar end groups relative to one another in such a way as to reduce the resultant moment. In trimethylene bromide it is possible for the bromine atoms to approach each other closely enough so that van der Waals forces operate to compensate in part for the dipole repulsions, thus favoring to a greater extent configurations in which the dipoles point in the same direction.⁸ The effect of the relative stabilization of such rotational isomers of high dipole moment is to give trimethylene bromide a higher moment than one would expect if only dipole forces were operative. Apparently the same factors obtain in the Schiff bases derived from trimethylenediamine.

As expected, the dipole moment of bis-acetylacetone-tetramethylenediimine (3.93 D), was found to be larger than that of bis-acetylacetoneethylenediimine (3.16 D). It has been noted¹¹ that the substitution of a benzoylacetone for an acetylacetone residue in both copper(II) and nickel(II) Schiff base chelates has only a small effect on the observed dipole moments. It seems reasonable, therefore, to assume that the dipole moments of the benzoylacetonyl and acetylacetonyl groups in the ligands have the same relative values as those reported for acetophenone and acetone (2.88 and 2.72 D , respectively¹²). If this assumption is correct, then the relative dipole moment values of bis-acetylacetone-tetramethylenediimine (3.93 D) and bis-benzoylacetone-tetramethylenediimine (3.81 D) are quite reasonable, since the greater polarity of the aromatic ketone would result in the subtraction of the component of its dipole moment increment from the group moments of the hydrogen bonded chelate rings. The effect would be further decreased by a possible slight steric factor which would change the statistical distribution of rotatory isomers slightly in favor of the *trans* forms. The apparent reversal of these effects for bisbenzoylacetoneethylenediimine (3.21 D) and bisacetylacetoneethylenediimine is within experimental error and is not considered significant. As indicated above, the *trans* forms contribute proportionately more in the ethylene-

(10) H. Eyring, *THIS JOURNAL*, **54**, 3191 (1932).

(11) P. J. McCarthy, Ph.D. Dissertation, Clark University, Worcester, Mass., 1955.

(12) "The Structure of Molecules," Y. K. Syrkin and M. E. Dyatkina, Butterworths Scientific Publications, London, 1950, p. 228.

(7) C. P. Smyth and W. S. Wall, *THIS JOURNAL*, **54**, 2261 (1932).

(8) C. P. Smyth and W. S. Wall, *J. Chem. Phys.*, **1**, 200 (1933).

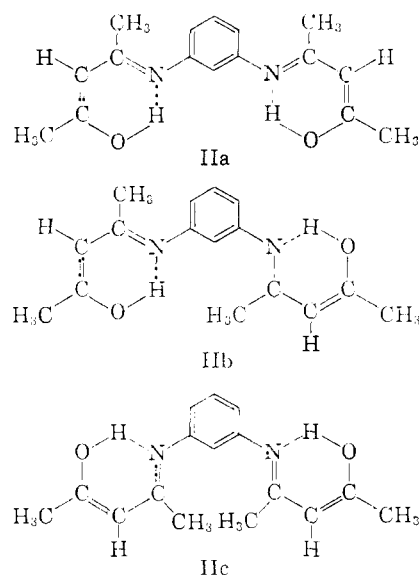
(9) P. Trunel, *Ann. chim. (Paris)*, [11] **13**, 93 (1939).

diamine derivatives, and the benzene rings therefore have very little influence, both sterically and electronically, on the molecular moment. The differences between the behavior of the ethylene and trimethylene compounds, with respect to the replacement of methyl by phenyl, is outside experimental error, and is in the direction that would be observed if the increased van der Waals forces between the phenyl groups favored rotational forms having the *cis* configuration.

The structure of bis-acetylaceton-*m*-phenylenediimine differs considerably from those of the other ligands discussed here. As can be seen from structures IIa,b,c rotation is restricted to the two carbon-nitrogen single bonds. The bulky and relatively rigid *m*-phenylene bridge should likewise limit the number of configurations of the end groups favoring *trans* forms and a relatively low dipole moment. However, the relatively high moment observed seems to indicate a constitutional factor which favors a higher moment. This factor may well be the tendency of the aromatic ring to conjugate with the hydrogen bonded chelate rings to stabilize three forms, *cis-cis*, *cis-trans* and *trans-trans*, as is indicated by formulas IIa, IIb and IIc.

The contributions of two of these, IIa and IIc, which have high moments, could easily account for the high observed moment.

The dipole moments of bis-trifluoroacetylacetonpropylenediimine (5.70 *D*), bis-*p*-bromobenzoylacetonpropylenediimine (3.99 *D*) and bis-*m*-nitrobenzoylacetontrimethylenediimine (6.96 *D*)



are several Debye units higher than the corresponding unsubstituted ligands. This effect is probably the result of the fact that the polar group moments lie in an average direction such that they add to the moments due to the hydrogen-bonded chelate rings. As expected, this factor outweighs the tendency for the average orientation of the end dipoles in the more polar ligands to be somewhat closer to the *trans* form because of the mutual repulsive forces between them.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY AT HARVARD UNIVERSITY]

Cyclooctatetraene Iron Tricarbonyl and Related Compounds^{1,2}

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From the reaction between iron pentacarbonyl and cyclooctatetraene the three solid compounds $C_8H_8 \cdot Fe(CO)_3$ (I), $C_8H_8 \cdot [Fe(CO)_3]_2$ (II) and $C_8H_8 \cdot Fe_2(CO)_7$ (III) have been isolated and characterized. Compound I is appreciably volatile and essentially air stable. Its nuclear magnetic resonance spectrum shows a single proton resonance, and it cannot be hydrogenated under conditions under which other metal-cyclooctatetraene complexes (*e.g.*, $C_8H_8 \cdot PtI_2$) readily absorb hydrogen. These and other properties suggest that all four double bonds of the C_8H_8 ring in I are involved in the bonding to iron. Compound I may also be prepared by heating cycloheptatriene-iron dicarbonyl with cyclooctatetraene. Compound II has no bridging carbonyl groups, and the $Fe(CO)_3$ groups must be on either side of the C_8H_8 ring. Compound III, however, is a derivative of $Fe_2(CO)_8$, possessing bridging carbonyl groups. Certain aspects of the infrared and ultraviolet spectra of I, II and III are discussed. The reaction between iron pentacarbonyl and a mixture of cyclooctatrienes has been investigated. A yellow-orange liquid complex $C_8H_{10} \cdot Fe(CO)_3$ (IV) was isolated. Its infrared and ultraviolet spectra and its probable constitution are discussed. The reaction between I and the compounds $(C_8H_8)_2M$ ($M = P, As$ and Sb) has been studied. The compounds $[(C_8H_5)_3P]_2Fe(CO)_3$, $(C_8H_5)_3As(C_8H_8)Fe(CO)_2$ and $(C_8H_5)_3Sb(C_8H_8)Fe(CO)_2$ have been isolated. Triphenylphosphine and IV, and triphenylphosphine and $C_8H_8 \cdot Fe(CO)_3$ afforded $[(C_8H_5)_3P]_2Fe(CO)_2$. The latter material was also obtained, together with $[(C_8H_5)_3P]_2Fe(CO)_3$, when cycloheptatriene-iron dicarbonyl was heated with triphenylphosphine.

The chemistry of the transition elements has been greatly expanded during the last decade by the preparation of derivatives of the metal carbonyls, in which carbon monoxide groups are replaced to some extent by other ligands. For the synthesis of these substituted metal carbonyls two

main preparative routes have been used: treatment of a metal carbonyl with the appropriate ligand and treatment of a compound of the metal with carbon monoxide. At this time perhaps the most remarkable of all the ligands occurring bonded to a metal simultaneously with CO are the unsaturated hydrocarbons which do so by means of their π -electrons. One extreme of such behavior is found in the sandwich bonds⁴ of the cyclopenta-

(1) Presented before the 136th Meeting of the American Chemical Society in Atlantic City, N. J., September 1959.

(2) For a preliminary communication see: T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 90 (1959).

(3) National Science Foundation predoctoral fellow 1958-1959.

(4) H. H. Jaffe, *J. Chem. Phys.*, **21**, 157 (1953); W. Moffitt, *This Journal*, **76**, 3388 (1954); J. D. Dunitz and L. E. Orgel, *J. Chem.*