with lead placed somewhere between zinc and magnesium.

The relative order obtained from a consideration of frequency shifts is

$$\mathrm{Cu} > \mathrm{Mg} > \mathrm{Ni} > \mathrm{Co} > \mathrm{Zn, Cd, Mn} > \mathrm{Pb}$$

The order is practically the same as the usual stability order of divalent metal ions[18] and also that found by Charles and Freiser.[19] The most notable difference is the variance in the position of magnesium. The anomalous magnitude of the frequency shift in the magnesium chelate might be related to the relatively low mass of magnesium.

The same type of shift for this peak has also been observed for the chelates of 2-(*o*-hydroxyphenyl)-derivatives of benzimidazole, imidazoline, benzothiazole and benzothiazoline.

In each series the copper chelate, which is the most stable of the reagent–metal complexes, has its 1250 kayser absorption peak at the highest frequency, while the zinc chelate, which is generally less stable than that of the nickel or cobalt, is at the lowest frequency. This behavior is very similar to that observed for the chelates of 8-hydroxyquinoline and derivatives.[20]

Acknowledgment.—The authors are indebted to Professor Mary E. Warga of the Physics Department for the use of the infrared spectrometer and to Professor Alfred Berger of the Engineering Department for the use of the press. They gratefully acknowledge the financial assistance of the U. S. Public Health Service.

[20] R. G. Charles, H. Freiser, R. Friedel, L. E. Hilliard and W. D. Johnston, *Spectrochimica acta*, **8**, in press (1956).

PITTSBURGH, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

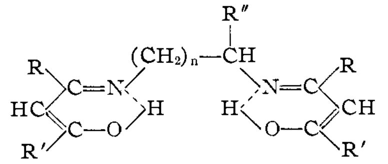
Dipole Moments of Metal Chelate Compounds. I. Analog of Bisacetylacetone-ethylenediimine[1]

BY PAUL J. MCCARTHY AND ARTHUR E. MARTELL

RECEIVED JANUARY 31, 1955

Dielectric constants of benzene solutions of bisacetylacetone-ethylenediimine, bisacetylacetonepropylenediimine, bistrifluoroacetylacetone-ethylenediimine, bisbenzoylacetone-ethylenediimine, bisbenzoylacetonepropylenediimine and bisbenzoylacetonetrimethylenediimine have been measured, and the values of the corresponding molar polarizations and dipole moments are reported. The magnitudes of the dipole moments are interpreted in terms of rotation of two hydrogen-bonded chelate rings about the alkylene bridge.

This is the first of a series of research reports on the dipole moments of chelating agents and metal chelate compounds. The analogs of bisacetylacetone-ethylenediimine were chosen as promising reagents with which to begin this program because the structures involved are relatively simple, and because many of the corresponding metal chelate compounds are soluble in benzene. The tetradentate ligands synthesized for this investigation are summarized in formula I. The names of the compounds, the substituents R, R′ and R″, and the values of *n* are given in Table I.



I

TABLE I

LIGAND STRUCTURES

n	R	R′	R″	Name of ligand
1	CH_3	CH_3	H	Bisacetylacetone-ethylenediimine
1	CH_3	CH_3	CH_3	Bisacetylacetonepropylenediimine
1	CH_3	CF_3	H	Bistrifluoroacetylacetone-ethylenediimine
1	C_6H_5	CH_3	H	Bisbenzoylacetone-ethylenediimine
1	C_6H_5	CH_3	CH_3	Bisbenzoylacetonepropylenediimine
2	C_6H_5	CH_3	H	Bisbenzoylacetonetrimethylenediimine

Of these substances, only the parent compound, bisacetylacetone-ethylenediimine has been previously reported.[2] The trifluoro derivative also has been prepared by Martell, Belford and Calvin.[3]

Experimental

Apparatus.—A sensitive heterodyne-beat apparatus was set up with a variable-frequency oscillator and a crystal-controlled, fixed-frequency oscillator, both of which were fed into a stable receiver with a loudspeaker as detector. Since the beats near the null point were clearly audible, good precision (1 part in 10^6) was obtained in all capacitance measurements. The fixed-frequency oscillator was constructed according to the circuit of the Blily Model 1C oscillator, with modification which allowed the use of the oscillator at 100 kc. per second as well as the normal operating frequencies of 500 and 1000 kc. per second. The receiver was a National HRO "60" model. The variable-frequency oscillator was a frequency meter, BC-221-T, made by the Zenith Radio Corporation for the Army Signal Corps. A General Radio Type 722-D 1100 $\mu\mu$f. precision condenser was connected to the frequency meter in parallel with the experimental dielectric constant cell. The precision condenser was internally calibrated at 10 $\mu\mu$f. intervals in a manner similar to that suggested by Smyth.[4] The corrections were plotted against readings of the condenser and were used to correct all subsequent capacitance measurements.

The glass dielectric constant cell contained three rigidly-mounted platinum cylinders, spaced 0.07 cm. apart. The inner and outer cylinders were connected together and

---

[1] (a) Abstracted from a dissertation submitted by Paul J. McCarthy, to the Faculty of Clark University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) This work was supported by a grant from Research Corporation and by the Office of Ordnance Research under Contract No. DA19-020-ORD-3243.

[2] A. Combes and C. Combes, *Compt. rend.*, **108**, 1252 (1889).

[3] A. E. Martell, L. Belford and M. Calvin, unpublished results.

[4] C. P. Smyth, "Determination of Dipole Moments," in "Physical Methods of Organic Chemistry," A. Weissberger, Editor, Vol. I, Part II, Interscience Publishers, New York, N. Y., 1945, pp. 1005 ff.

TABLE II

Compound	ϵ_1	α	v_1	$-\beta$	P_E (cc.)	$P_{2\infty}$ (cc.)	μ (D)
Bisacetylacetone-ethylenediimine	2.2728	4.989	1.14489	0.1866	64.62	274.52	3.16 ± 0.03
Bisacetylacetonepropylenediimine	2.2707	4.273	1.14538	.2122	69.27	258.00	2.98 ± .04
Bistrifluoroacetylacetone-ethylenediimine	2.2737	11.065	1.14537	.4426	63.26	761.15	5.82 ± .02
Bisbenzoylacetone-ethylenediimine	2.2711	3.495	1.14496	.2339	103.60	323.74	3.21 ± .05
Bisbenzoylacetonepropylenediimine	2.2730	1.993	1.14513	.2221	108.25	235.56	2.39 ± .07
Bisbenzoylacetonetrimethylenediimine	2.2711	4.496	1.14535	.2887	108.25	399.34	3.71 ± .04

grounded, while the middle one was connected to the variable-frequency oscillator by means of a rigid shielded cable. Temperature control was obtained by clamping the cell in a fixed position in a constant-temperature oil-bath. Solutions were introduced and removed through a capillary tube without removing the cell from the bath.

The replaceable capacitance of the cell, C_R, was determined from the quantity $(C_B - C_A/(\epsilon_B - \epsilon_A)$, where the quantities C_B and C_A are the measured cell capacitances with substances B and A as dielectrics, and ϵ_B and ϵ_A represent the corresponding dielectric constants. After a series of measurements with dry nitrogen and purified benzene, C_R was found to be 192.05 ± 0.02 $\mu\mu$f. at 25.25°. The dielectric constants of benzene and dry nitrogen at this temperature were taken to be 2.2722[5] and 1.0005_3,[6] respectively.

Materials.—For all solution measurements, J. T. Baker C.P.benzene was purified in the following way. After successive washings with concentrated sulfuric acid and sodium hydroxide solution, it was washed repeatedly with water. After it was dried over calcium hydride, it was fractionally crystallized; the first solid (about 15%) and the last liquid (15–20%) were rejected. It was then refluxed over calcium hydride and distilled through a Widmer column, the first and last fractions (about 15% each) again being rejected. The benzene used for calibration was subjected to additional washings with water and a second crystallization.

The preparation of the ligands used in this investigation, and the problems involved, have been discussed in a previous publication.

Measurements.—Density measurements were made with 25-ml. Rieschauer pycnometers calibrated with gas-free distilled water. For all weighings of liquids, the usual corrections for buoyancy and vapor pressure were made. Solutions were made up to the desired concentration in a separate flask, and portions were then pumped into the pycnometer and into the experimental dielectric constant cell.

About one hour after turning on the oscillators, the capacitance of the cell containing dry nitrogen was determined. Some of the solution was then admitted into the cell, and the capacitance was again determined after temperature equilibrium had been obtained. After the capacitance had been measured, the cell was washed in position with benzene and dried with a stream of dry nitrogen. All capacitance measurements were made at a frequency of 1000 kc. per second.

Calculations.—The molar polarization of the solute at infinite dilution ($P_{2\infty}$) was determined by the method of Halverstadt and Kumler.[7] Plots of the dielectric constants (ϵ_{12}) and specific volumes (v_{12}) of the solutions against the weight fractions (w_2) of the solute were found in all cases to be linear for $w_2 \leqq 0.01$. The values of the intercepts were in most cases very close to the values of the dielectric constant and specific volume of pure benzene. $P_{2\infty}$ was calculated 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_{12} against w_2, β and v_1 are the slope and intercept of the plot of v_{12} against w_2, and M_2 is the molecular weight of the solute. The parameters of all straight lines were calculated by the method of least squares.

The value of P_E, the electron polarization, was determined by summing the bond refractivities; for this the table of Vogel[8] was used. The quantities thus obtained for the ligands used in this investigation are listed in Table II. In all compounds the enol form was assumed to predominate, for reasons given below. The error resulting from the small amount of keto form present would be made negligible by a compensating exaltation resulting from internal hydrogen bonding (chelation).

The atom polarization of many organic compounds have been found to be from 5 to 10% of the electron polarization. For the compounds investigated the upper value seemed more probable as a consequence of the presence of two hydrogen-bonded chelate rings. Accordingly, the value 10 ± 5% P_E was used as the probable value of P_A.

For the conditions employed, the dipole moment, μ, is equivalent to $0.01281\sqrt{P_0T}$, where T is the absolute temperature, and P_0, the orientation polarization, is evaluated by subtracting P_E and P_A from $P_{2\infty}$. Evaluation of μ from the slope of a plot of $P_{2\infty}$ against $1/T$ gave erroneous results. This was probably due primarily to the limited temperature range (6–45°) in which the benzene solutions were measured.

Results

Table II contains the parameters calculated from experimental data gathered for the six compounds. In each case four or five solutions were measured. Values for $P_{2\infty}$ and μ were determined as outlined above. The listed errors in the μ values were calculated on the assumptions: (1) that errors in the atom and electron polarizations lie within the limits assigned, and (2) the values of $P_{2\infty}$ were determined with relatively negligible errors. The errors listed thus represent the deviations resulting from uncertainties in the electron and atom polarizations. The absolute reproducibility of the results is not readily estimated from the experimental data. However, independent measurements by another investigator in this Laboratory indicate that the precision is within ±0.1 *D*.

Discussion

It may be assumed that the compounds investigated are almost completely enolized in benzene solution, since the enolized form is stabilized by intramolecular hydrogen-bond formation. Other compounds of this type have been found to be nearly completely enolized in the absence of polar solvents; for example, acetylacetone is 92% enolized in the non-polar solvent hexane[9] and benzoylacetone is 98–99% enolized in the liquid state.[10]

From a study of Fisher–Hirschfelder–Taylor molecular models of the compounds under discussion, it is clear that in all of them there is freedom of rotation about the C–C bond(s) of the bridge. Some of the compounds have freedom of rotation about the two C–N bonds as well, while in the other compounds this latter rotation is more or less limited by steric hindrance.

Models suggest that bisacetylacetonepropylenediimine may exist in two non-interchangeable spatial configurations which are determined by the relative positions of the methylene and two methyl

---

[5] L. Hartshorn and D. Oliver, *Proc. Roy. Soc. (London)*, **A123**, 664 (1929).

[6] A. Maryott and F. Buckley, National Bureau of Standards Circular #537, 1953, pp. 2f.

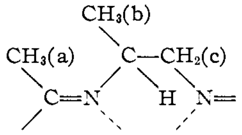
[7] I. Halverstadt and W. Kumler, THIS JOURNAL, **64**, 2988 (1942).

[8] A. Vogel, *Chemistry and Industry*, 358 (1950).

[9] J. B. Conant and A. Thompson, THIS JOURNAL, **54**, 4039 (1932).

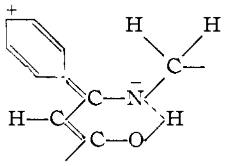
[10] G. E. Branch and M. Calvin, "The Theory of Organic Compounds," Prentice-Hall, Inc., New York, N. Y., 1941, p. 294.

groups shown in formula II. In one of these configurations, rotation about the C–N bond adjacent to the bridge methyl is restricted to about 160°, while rotation about the other C–N bond is restricted to about 270°. In the other configuration, in which $-CH_3$ (a) is spatially trapped between $-CH_3$ (b) and $-CH_2$ (c), rotation is restricted to approximately 45 and 270° for the same bonds, respectively. In bisacetylacetone-ethylenediimine, on the other hand, rotation about both C–N bonds appears to be limited to about 270°. The complexity of the various rotations together with the lack of adequate knowledge of individual bond moments makes it impossible to predict the results these steric effects will produce on the resultant dipole moments of these two molecules. However, it seems possible that the substitution of a methyl group for a bridge hydrogen could cause the change in dipole moment observed (0.18 *D*), because of the steric effects indicated.

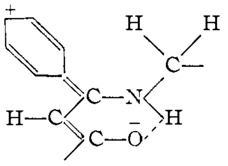


II

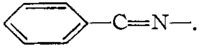
The substitution of a phenyl group for a methyl group is often accompanied by a change in dipole moment, due to the contribution of ionic resonance forms to the structure of the molecule. The similarity in dipole moment between bisacetylacetone-ethylenediimine and bisbenzoylacetone-ethylenediimine suggests that ionic resonance forms like those shown in formulae III and IV contribute little to the structure of the latter compound. Lack of coplanarity between the phenyl groups and the chelate rings is probably the reason for this. The lack of coplanarity in turn can be explained by steric repulsion between the phenyl radical and the adjacent hydrogen atoms shown in III and IV. When a phenyl group is adjacent to the bridge, models indicate that the smallest angle possible between the plane of the phenyl group and the plane of the chelate ring is about 35°. When a phenyl group is at the end of the molecule, no steric repulsion hinders coplanarity. In this latter case one would expect the substitution of a phenyl for a methyl group to cause a significant change in the dipole moment.



III



IV

The position of the phenyl groups is substantiated by the following evidence. The acid dissociation constants of acetylacetone (pK = 9.7) and benzoylacetone (pK = 9.8)[11] show that the electron-releasing power of the phenyl group is slightly greater than that of the methyl group. Enolization of the acetyl oxygen will therefore be favored over that of the benzoyl oxygen, and Schiff base formation will occur adjacent to the phenyl groups. This result is corroborated by the fact that aromatic Schiff bases are known to form much more readily than aliphatic Schiff bases.[12] The former are stabilized by the resonance energy of the system  Aliphatic Schiff bases have no such resonance stabilization; some of them are accordingly rather unstable and difficult to prepare. One might then expect that in molecules containing an aromatic and an aliphatic residue, either of which can form a Schiff base, the Schiff base would form with the aromatic part.

In view of this discussion, the difference in moment (0.59 *D*) between bisacetylacetonepropylenediimine and bisbenzoylacetonepropylenediimine can best be ascribed to steric effects caused by the proximity of the two phenyl groups and the bridge methyl group in the latter compound.

A similar solution is also probable for the case of bisbenzoylacetonetrimethylenediimine (μ = 3.71 *D*), bisbenzoylacetone-ethylenediimine (μ = 3.21 *D*), and bisbenzoylacetonepropylenediimine (μ = 2.39 *D*). From models it appears that movement of one part of the molecule in reference to the rest is more difficult and encumbered as one changes the bridge from trimethylene– to ethylene– to propylene–. The number of possible configurations is decreased in this same order because of increased steric repulsions. The noticeable differences in moment should therefore be attributed to these steric effects.

Bistrifluoroacetylacetone-ethylenediimine has its $-CF_3$ groups at the ends of the molecule. The strong electrophilic character of the $-CF_3$ group leads to the enolized form $CF_3-C(OH)=CHCO-CH_3$. Schiff base formation consequently takes place at the carbonyl adjacent to the $-CH_3$ group. The fact that this compound has a dipole moment 2.66 *D* greater than bisacetylacetone-ethylenediimine shows that the $-CF_3$ group moments lie in the same general direction as the moment of the rest of the molecule. This also means that the $-CF_3$ groups must be at the ends of the molecule.

WORCESTER, MASS.

---

[11] M. Calvin and K. Wilson, THIS JOURNAL, **67**, 2005 (1945).

[12] W. Emerson, "The Preparation of Amines by Reductive Alkylation," in "Organic Reactions," Vol. IV, R. Adams, Editor, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 190 f.