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Seven-Coordination and Ligand-Repulsion Models for Bond Geometry

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Received October 16, 1967

A simple and attractive model which has been applied for prediction of geometries of small molecules is that of mutually repulsive points on a spherical surface. For seven groups about a common center the favored geometry depends upon the power of n appearing in the energy expression $E = \Sigma r_{ij}^{-n}$. For $n < 2.5$ a D_{5h} symmetry is favored but out-of-plane puckerings of the equatorial atoms require very little energy. For high n a C_{3v} structure is stable. At intermediate values of n, C_2, C_s, and C_{2v} symmetries are of importance. Comparison with experimentally determined structures for IF_7 and XeF_6 suggests that, for a large central atom, a relatively low value of n ($\leqslant 3$) is more appropriate than a high value. The comparison also serves to warn that the points-on-a-sphere model must be applied with caution in cases involving more than six ligands.

Several models of directed valence have received attention which rely for the prediction of bond direction solely upon the mutual repulsion of ligands or electron pairs. The valence shell electron pair repulsion model of Gillespie and Nyholm[2] is perhaps most widely known, but others such as the nuclear repulsion approach of Gray and Pritchard[3] have been discussed. One approach[3,4] to models of this type is the examination of the behavior of a number of points confined to the surface of a sphere, under an energy law of the form

$$E = \sum_{i \neq j} r_{ij}^{-n} \tag{1}$$

where r_{ij} is the distance between two of the points, and n is a constant. For any number of particles (ligands) less than seven, the arrangement of lowest energy is known to be the same for any positive value of n, so that the structural predictions of the various repulsion models are not ambiguous on this score. Recently, however, models with seven-coordination have occasioned interest, among them IF_7 and (for Gillespie's model) XeF_6. In order to evaluate the success of the various point-repulsion models in these cases, it is essential to have a clear understanding of the stable arrangement of seven points on a sphere. Prior work on this problem[4] is not as complete as might be desired and is in some respects misleading, as will be shown below. The calculations reported here were begun in connection with investigations of the structures of IF_7 and XeF_6. The results have implications in view of the experimental structures.

Calculations

The calculations were carried out using a FORTRAN computer program previously described,[5] which was designed to find the minimum energy configuration by a Gauss–Newton procedure for a molecular frame under a specified molecular force field. While this program was more than adequate for the present problem in terms of versatility of description for the molecule and the force field, difficulty with convergence was encountered in some cases, particularly in the neighborhood of C_s and D_{5h} symmetries. Investigation of several of these cases indicated that the source of trouble was the form of the potential energy minimum. In certain directions from the minimum in the multidimensional parameter space of this problem, the potential was not quadratic, but more nearly quartic in form. This would lead to difficulties also in the force–equilibrium procedure employed by Claxton and Benson.[4] We used two procedures to overcome this problem. First, a provision had been included in the computer program to multiply the correction vector in molecular parameter space by a scalar, S, found by the equation

$$S = \frac{V_1 + 3V_0 - 4V_{1/2}}{4V_1 + 4V_0 - 8V_{1/2}} \tag{2}$$

where V_0 was the energy from the previous minimization cycle, V_1 was the energy for the configuration resulting upon application of the correction vector, and $V_{1/2}$ was the energy upon application of half the correction vector. For most problems involving hydrocarbons and anharmonic Urey–Bradley potentials, the value of S had been in the neighborhood of unity, and limits on S of -1 and 2 had been established within the program. In the present case it appeared advisable to increase the upper limit to 8 or 10, after which values of 3–6 for S were not uncommon. Convergence was somewhat speeded by this device but, since eq 2 is most appropriate for a quadratic minimum, it is not surprising that the process was slow.

In all cases where slowness of convergence was encountered, a second procedure was applied. This consisted of a point-by-point survey of energies in the vicinity of the presumed energy minima. In some instances this led to small corrections in the reported parameters.

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[2] R. J. Gillespie and R. S. Nyholm, *Quart. Rev.* (London), **11**, 339 (1957); R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963).

[3] B. F. Gray and H. O. Pritchard, *J. Chem. Phys.*, **25**, 779 (1956); see also discussion in this reference.

[4] T. A. Claxton and G. C. Benson, *Can. J. Chem.*, **44**, 157 (1966), and earlier work cited therein.

[5] E. J. Jacob, H. B. Thompson, and L. S. Bartell, *J. Chem. Phys.*, **47**, 3736 (1968).

Results and Discussion

Minimum energies for points on a sphere of unit radius are given in Table I for various symmetries. Since eq 1 contains no multiplicative constant, the energy is in arbitrary natural units. To permit ready comparison over a range of values of n, all energies were divided by the energy of the C_{3v} form. The results are displayed in Figure 1. Tables II–V give the equilibrium geometric parameters for various symmetries as a function of n.

TABLE I

ENERGIES FOR VARIOUS SYMMETRIES AND POTENTIAL FUNCTIONS

Exponent n	Energy D_{5h}	C_2	C_s	C_{2v}	C_{3v}
0.5	17.3530			17.3552	17.3555
1.0	14.4530	[D_{5h}]	[D_{5h}]	14.4579	14.4586
2.0	10.2500	[D_{5h}]	[D_{5h}]	10.2588	10.2601
2.5	8.7202	8.7202	8.7202		8.7305
3.0	7.4648	7.4641	7.4642	7.4718	7.4734
3.5	6.4268	6.4248	6.4247		6.4318
4.0	5.5625	5.5578	5.5578	5.5606	5.5620
4.5			4.8288		4.8305
5.0	4.2269	4.2102	4.2102	4.2102	4.2108
6.0	3.2656			3.2305	3.2300
9.0	1.6253			1.5364	1.5319
12.0	0.8383			0.7610	0.7539

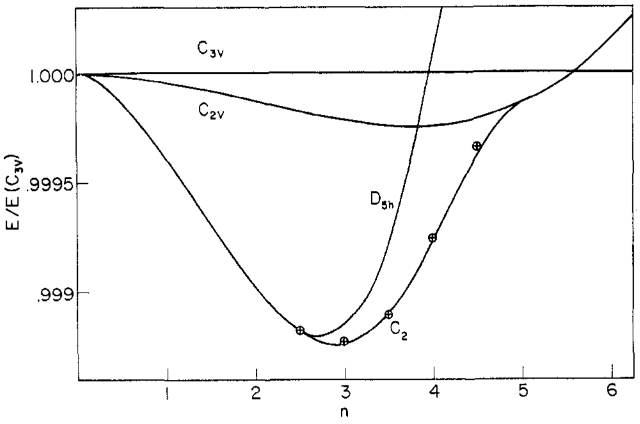

Figure 1.—Relative energies of seven points on a sphere, assuming a repulsive potential r_{ij}^{-n}. Data of Claxton and Benson[4] as well as those in this paper were used in constructing this figure. Energies for C_s structures are indicated by ⊕. The nearby solid curve is for C_2 structures.

As noted by Claxton and Benson, at any n value between 3 and 5.6 there is a C_2 structure more stable than either D_{5h}, C_{2v}, or C_{3v}. There is, however, also a C_s structure with essentially the same energy as the C_2. Just below $n = 2.5$, the stable C_2 and C_s geometries both become identical with that for D_{5h}. The C_2 geometry reported by Claxton and Benson for $n = 2$ is nearly D_{5h}, differing by virtue of a slight buckling of the five-ligand ring. On careful examination it was established that (a) this configuration is slightly higher in energy than D_{5h} and (b) there is no energy minimum at this C_2 geometry and no maximum between this and D_{5h}. The potential well at D_{5h} is, however, very flat and shallow, having a nearly quartic contour for buck-

TABLE II

STABLE GEOMETRIES FOR C_{3v}[a]

n	Deg θ_2	θ_5
0.5	73.2	128.6
1.0	73.3	128.8
2.0	73.5	129.1
2.5	73.6	129.2
3.0	73.8	129.4
3.5	73.9	129.5
4.0	74.1	129.7
4.5	74.2	129.8
5.0	74.4	130.0
6.0	74.6	130.3
9.0	75.3	130.9
12.0	75.8	131.4

[a] $\theta_1 = 0°$; $\theta_2 = \theta_3 = \theta_4$; $\theta_5 = \theta_6 = \theta_7$; $\phi_2 = 60°$; $\phi_3 = 180°$; $\phi_4 = 300°$; $\phi_5 = 0°$; $\phi_6 = 120°$; $\phi_7 = 240°$.

TABLE III

STABLE GEOMETRIES FOR C_{2v}[a]

n	Deg θ_2	θ_6	ϕ_2
0.5	80.9	144.2	49.1
1.0	80.8	144.2	49.0
2.0	80.6	144.0	49.0
3.0	80.3	143.9	48.9
4.0	80.0	143.7	48.8
5.0	79.7	143.5	48.8
6.0	79.4	143.3	48.7
9.0	78.7	142.9	48.7
12.0	78.3	142.6	48.7

[a] $\theta_1 = 0°$; $\theta_2 = \theta_3 = \theta_4 = \theta_5$; $\theta_6 = \theta_7$; $\phi_2 = -\phi_3 = 180° + \phi_4 = 180° - \phi_5$; $\phi_6 = 0°$; $\phi_7 = 180°$.

TABLE IV

STABLE GEOMETRIES FOR C_2[a]

n	Deg θ_2	θ_4	θ_6	ϕ_2	ϕ_4
2.0[b]	72	90	144	2[b]	93[b]
2.5	72	90	144	6	94
3.0	72	89	144	12	99
3.5	73	88	144	19	104
4.0	74	87	144	27	111
4.5	77	84	144	37	120
5.0	79	80	144	48	130
6.0	79	79	143	49	131

[a] $\theta_1 = 0°$; $\theta_2 = \theta_3$; $\theta_4 = \theta_5$; $\theta_6 = \theta_7$; $\phi_3 = 180° + \phi_2$; $\phi_5 = 180° + \phi_4$; $\phi_6 = 0°$; $\phi_7 = 180°$. [b] Essentially D_{5h}. The energy of the geometry given was identical to eight significant figures with that of D_{5h}, and no intervening maximum was found.

TABLE V

STABLE GEOMETRIES FOR C_s[a]

n	Deg θ_2	θ_4	θ_6	θ_7	ϕ_2	ϕ_4
2.0	88	91	93	180	72	144
2.5	87	91	94	180	72	144
3.0	84	91	101	177	71	143
3.5	83	91	102	176	70	143
4.0	81	90	107	173	69	143
4.5	81	89	111	171	68	142
5.0	79	80	142	145	50	132
6.0	80	80	143	143	49	131

[a] $\theta_1 = 0°$; $\theta_2 = \theta_3$; $\theta_4 = \theta_5$; $\phi_3 = -\phi_2$; $\phi_4 = -\phi_5$; $\phi_6 = 0°$; $\phi_7 = 180°$.

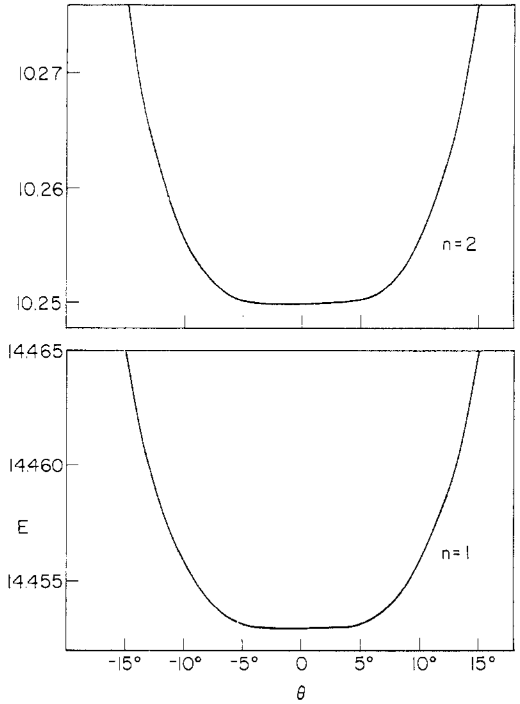

Figure 2.—Energy-well contour for small equatorial buckling distortions from D_{5h}. The distortion coordinate θ is defined in the text. This contour is identical for the two distortions to within any difference demonstrable on the scale of this figure.

ling along either a C_2 or a C_s symmetry coordinate. Figure 2 shows this contour as a function of the symmetry coordinate θ, where θ is related to the polar coordinates of the five nearly equatorial atoms (indexed by the integer k) by

$$\theta_k = (\pi/2) + \theta \sin \phi_k$$

for C_2 symmetry and

$$\theta_k = (\pi/2) + \theta \cos \phi_k$$

for C_s symmetry where

$$\phi_k = 2\pi k/5$$

For small distortions from D_{5h} the two symmetries give the same energies. The ring-buckling mode is thus degenerate for small amplitudes and is an instance of pseudo-rotation analogous to that found in other five-membered rings. Above $n = 5.6$ the stable geometries for both C_2 and C_s become identical with that for C_{2v}. Throughout the region $n = 2.5$–5.6 convergence of the program was slow. Further, as is evident from the vertical scale of Figures 1 and 2, the energy differences between symmetries are only a very small portion of the total energy. Thus, a number of the equilibrium coordinates for C_s and C_2 in Tables IV and V are of relatively low precision. For the C_s case, in particular, structures differing in energy by only 1 ppm often covered a wide range of geometries. There seemed little economic value in the expenditure of computer time to acquire more precise figures.

Conclusions

Insofar as the points-on-a-sphere model has validity for the description of molecular geometries, the stable configuration for seven-coordination does, indeed, depend on the value of n assumed. D_{5h} is the stable geometry for n less than approximately 2.5, and the corresponding potential function for the ring-buckling distortions is far from quadratic in form when $n \gg 1$. Experimentally, one AB_7-type molecule, iodine heptafluoride, has been studied adequately in the vapor phase.[6] The molecule has a D_{5h} equilibrium structure and exhibits large out-of-plane vibrational amplitudes. Therefore, in an application of the present model to other higher coordination structures, a value of n less than 3 is presumably indicated. In this connection it should be noted that, while the structures of various symmetries differ in energy by only a few parts per 10,000 at low n, D_{5h} is higher than the others by nearly 1% at $n = 6$ and by 11% at $n = 12$. This fact reinforces the original interpretation of the valence shell electron pair repulsion model to the effect that repulsions originate principally from bond orbital interactions imposed by the exclusion principle rather than from simple steric forces between ligands themselves. A steric (nonbonded) repulsion model of the usual type involving a hard repulsive potential (n the order of 10) will *not* account for the experimental IF_7 structure.

A qualitative success of the pair-repulsion model as used by Gillespie was its prediction[7] of a nonoctahedral structure for XeF_6. Although the pair-repulsion model considerably overemphasizes the tendency of XeF_6 to distort from O_h symmetry,[8] the model does provide a rationale for the characteristic differences between XeF_6 (with seven valence pairs) and TeF_6 (with six valence pairs). The tellurium hexafluoride molecule is a fairly rigid regular octahedron.[9] Xenon hexafluoride, on the other hand, is an extremely flexible molecule,[10] in accord with the very low energy differences predicted by the present model for structures of different symmetry at low n values. Indeed, because of the large amplitudes of vibration, it has not yet been possible to establish, from diffraction or spectroscopic evidence, whether the potential energy function has minima at non-O_h configurations corresponding to a stereochemically active lone pair avoiding the bonding pairs, or whether the minimum is at O_h but is so shallow that the restoring force for t_{1u} deformations is nearly zero.

The quantitative failure of the pair-repulsion model in its prediction of the structure of XeF_6 is scarcely surprising in view of the nonequivalence of the seven

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valence pairs and in view of the naiveté of the model itself. Nevertheless, the observed nonequivalence between the lone pair and bonding pairs is not in the direction predicted by Gillespie's rules,[2] since the lone pair of xenon occupies a much smaller portion of the valence shell than do the bonding pairs to fluorines. It is possible that a model in which the effective value of *n* depends upon molecular environment could extend the utility of the present model. We must conclude, however, that the points-on-a-sphere model has at best a limited utility for geometries with more than six ligands.

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Coordination Compounds of 2,5-Dithiahexane 2,5-Dioxide

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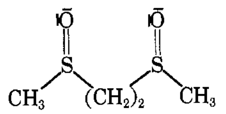
Received October 16, 1967

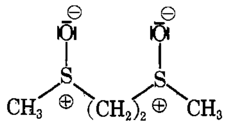
A number of coordination compounds of 2,5-dithiahexane 2,5-dioxide ($DTHO_2$) with transition metal salts have been synthesized, and their structures were determined by chemical analyses, infrared spectra, electronic absorption spectra, X-ray diffraction patterns, and magnetic susceptibility measurements. Compounds containing the complex cations $[M(DTHO_2)_3]^{2+}$ ($M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$, and Cd^{2+}) and the compounds $[Pd(DTHO_2)Cl_2]$ and $[Pt(DTHO_2)Cl_2]$ are reported.

Introduction

Dimethyl sulfoxide (DMSO) is known to form coordination compounds with several metal ions. Their preparation, properties, and various physical characteristics have been reported.[2-7] The present paper describes the results of a similar study on the compounds of 2,5-dithiahexane 2,5-dioxide ($DTHO_2$) with some metals of the transition series, namely, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pd^{2+}, and Pt^{2+}, as well as Zn^{2+} and Cd^{2+}. In all of the known metal complexes of DMSO except Pd^{2+} and Pt^{2+}, coordination takes place through the oxygen atom, and the same was to be expected for $DTHO_2$. The bidentate ligand, $DTHO_2$, whose structure is best represented by I and II, can form a seven-membered ring around a single metal ion.[8,9]



I



II

Because there are no known reports describing the donor properties of $DTHO_2$ and its complexes with metal ions, we undertook this study. Upon examination of the magnetic and spectral properties of the complexes of the transition metals, one concludes that the compounds are quite similar to DMSO complexes. The bidentate nature of the ligand is confirmed, and, as would be expected, $DTHO_2$ gives rise to a stronger ligand field than that of DMSO. Since the ligand has two equivalent asymmetric sulfur atoms, it exists in *dl* and *meso* modifications. Conclusive evidence is not available to indicate whether the high-melting (α) modification used in this work is the internally compensated *meso* isomer or the racemic *dl* mixture. Tris-chelate complexes of either the *meso* or *dl* form of $DTHO_2$ could occur as two pairs of optical enantiomorphs. The problem of separation and resolution of stereoisomers will be left for future investigation.

Experimental Section

All materials were of at least reagent grade. The compound 2,5-dithiahexane (DTH) was obtained from Aldrich Chemicals and was used in the preparation of $DTHO_2$ without further purification.

Analytical Procedures.—Perchlorates were determined by precipitation with nitron.[10] Carbon, hydrogen, and chloride analyses were performed by Weiler and Strauss, Microanalytical Laboratory, Oxford, England. Metal analyses were determined by EDTA titration.[11]

Preparation of Compounds.—The ligand $DTHO_2$ was synthesized from DTH. The α isomer, mp 166° (lit.[12] 164°), prepared by a method to be reported,[13] was used in this investigation.

Unless otherwise indicated, all complexes of $DTHO_2$ were prepared as follows.

Cobalt(II) perchlorate hexahydrate, $Co(ClO_4)_2 \cdot 6H_2O$ (0.732 g, 0.002 mole), was dissolved in 5 ml of methanol. To this solution was added $DTHO_2$ (0.924 g, 0.006 mole) dissolved in 15 ml of methanol. Immediate precipitation of a rose-pink crystalline material occurred after mixing the two solutions. The product

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[1] Undergraduate Research Participant, Summer, 1966.

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