

(0.005) Å, respectively. These four dicyclopentadienyl compounds are also similar in their chemical reactivity; in contrast to, e.g., ferrocene and ruthenocene they react with air or moisture. The difference in the stability of the two classes of compounds is reflected in the vibrational amplitudes of the M—C distances; in the unstable compounds they are twice as large as in the stable ones;⁸ $u(\text{Fe—C})=0.062(0.001)$ Å and $u(\text{Ru—C})=0.060(0.001)$ Å.

It has been pointed out⁷ that the M—C bond distances in $(\text{C}_5\text{H}_5)_2\text{Sn}$, $(\text{C}_5\text{H}_5)_2\text{Pb}$, and $(\text{C}_5\text{H}_5)_2\text{Mn}$ can be calculated to 0.01 Å by adding the radius of the dipositive ion to a carbon atom radius of 1.58 Å. (The M—C distances in $(\text{C}_5\text{H}_5)_2\text{Fe}$ and $(\text{C}_5\text{H}_5)_2\text{Ru}$ are about 0.3 Å shorter than predicted by this rule.) One might therefore predict a Be—C bond distance in $(\text{C}_5\text{H}_5)_2\text{Be}$ of 1.89 Å. The reason why Be—C6 is so much longer than this is probably that the attraction between the beryllium atom and the second ring is compensated by van der Waals repulsion between the π -electron clouds in the two ligands; the vertical distance between the two cyclopentadienyl rings, 3.375(0.010) Å, is of the order of the van der Waals thickness of an aromatic ring. It appears reasonable then that the ligand rings are staggered in the equilibrium conformation. In $(\text{C}_5\text{H}_5)_2\text{Mn}$ where the ring-to-ring distance is 4.101(0.008) Å the rings appear to undergo virtually non-hindered rotation.⁷ In $(\text{C}_5\text{H}_5)_2\text{Fe}$ and $(\text{C}_5\text{H}_5)_2\text{Ru}$ the equilibrium conformation is eclipsed,⁸ but this is probably an effect of the strong metal-to-ring bonding.

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Equilibrium Constants and Model Testing from Spectrophotometric Data, using LETAGROP

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Spectrophotometric measurements have often been used for studying chemical equilibria, and methods for treating data for systems with several consecutive reactions have been given by J. Bjerrum, Olerup, Fronæus and others. These methods are limited to systems with mononuclear complex species, and when many complexes are involved, there is a certain risk of the accumulation of errors during the calculations. Computer methods for a least-squares treatment of spectrophotometric data have hitherto mainly been limited to reactions of the type $A+B\rightleftharpoons AB$. (For literature references, we refer to Rossotti and Rossotti¹ and to a forthcoming paper²).

We have recently made a version of the general minimizing program LETAGROP that allows a generalized least-squares treatment of spectrophotometric data, assuming any set of mononuclear or polynuclear species. The first application was to Teder's measurements on polysulfide solutions (components $\text{H}^+ + \text{S}^{2-} + \text{S}^0$). The program treats absorbance data (either absorbance E or apparent molar extinction coefficient, ϵ_B of one component), for any number N_λ of wavelengths (bands), and any number N_{soln} of solutions. The present version is designed for the two cases that have hitherto been the most frequent in the literature: 1) two components, the total concentrations of both in each solution are known, (A, B), 2) three components, the free concentration of one, and the total concentration of the two others in each solution are known (a, B, C). We can easily extend the treatment to cases (A, B, C) and (a, B, C, L) as the need arises.

The error square sum to be minimized is either that of the absolute errors, $(E_{\text{calc}} - E_{\text{exp}})$, or that of the relative

Table 1. Complex formation $\text{SCN}^-(\text{A}) + \text{UO}_2^{2+}(\text{B})$, data of Sten Ahrland 1949.³ Wavelengths λ_1 (366 nm, 9 solutions), λ_2 (436 nm, 30 solutions). ϵ_{10} (for SCN^-) negligible. In original, measured ϵ_{01} (for UO_2^{2+}) was subtracted from ϵ_{B} , hence given "e_{pq}" are $\epsilon_{11} - \epsilon_{01}$, $\epsilon_{21} - \epsilon_{01}$, $\epsilon_{31} - \epsilon_{01}$, and "e₀₁" is assumed to be 0 for λ_1 och λ_2 . The error limits (except for author's β) are σ values calculated by LETAGROP.

	Author's β		val=1 abs.errors	val=2 rel.errors
β_1	5.7(± 0.3)		5.37 ± 0.13	5.46 ± 0.11
β_2	5.5(± 1)		9.05 ± 1.5	9.06 ± 1.1
β_3	15(± 5)		6.4 ± 3.4	5.5 ± 3.2
λ_1				
ϵ_{11}	964 ± 17	975 ± 9	1005 ± 26	1001 ± 15
ϵ_{21}	3510 ± 1110	2740 ± 660	2490 ± 990	2140 ± 660
ϵ_{31}	3400 ± 5800	7500 ± 3700	1200 ± 19900	10100 ± 16600
λ_2				
ϵ_{11}	111.0 ± 0.8	108.45 ± 0.33	114.4 ± 0.7	111.7 ± 0.3
ϵ_{21}	308 ± 9	342 ± 7	217.4 ± 4.1	230.6 ± 3.6
ϵ_{31}	257 ± 7	227 ± 8	469 ± 13	486 ± 18
U_{abs}	5.75	—	4.45	—
$U_{\text{rel}} \times 10^4$		10.96	—	8.06
$\sigma(\text{rel.error})$		0.0058		0.0052

errors $(E_{\text{calc}} - E_{\text{exp}})/E_{\text{exp}}$; the choice is made by setting a control number $val=1$ or 2.

In the calculation, the variation of parameters is made at two levels. On an upper level, the equilibrium constants for the formation of various species are varied. For each set, k , of equilibrium constants the computer calculates, for each wavelength separately, the values for the molar extinctions that minimize the contribution to U from that wavelength, and the final result of the lower-level work is the lowest U value possible for that combination of equilibrium constants. Finally, from the set of points on the surface $U(k)$, the position k_0 of the minimum is calculated as usual in the LETAGROP programs and then tested.

The programs work quite fast. For each literature system we have been treating, only a couple of minutes' calculation on a CDC/3600 has been necessary.

As an example we give the results of LETAGROP treatment of Ahrland's data³ on thiocyanate-uranyl equilibria; note that the deviations in ϵ and β are σ (and not 3 σ). We do not pretend, in this or other cases, that "our" values for the equilibrium constants are better than those suggested by the ori-

ginal author but, at least, LETAGROP gives a fast and quite objective way of treating a large amount of spectrophotometric data. Combined with the judgment of the experimental worker this program should make it possible to get more precise information out of spectrophotometric data. Perhaps it might also be an incentive to increase the experimental accuracy still further, and to study more complicated systems by spectrophotometry.

It has been a pleasant surprise for us to notice how small standard deviations one may get on fitting good spectrophotometric data; for instance around 0.5% with the data given here.

The present LETAGROP version could also be applicable to other types of data with the same form of relationship between the measured quantity and the unknown parameters, as for spectrophotometric absorbance, $E = \sum \epsilon_i c_i$, for instance to other types of spectral data, and to conductance data.

More details are given in a paper to appear in *Arkiv Kemi*.²

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Tentatively Standardized Symmetry Coordinates for Vibrations of Polyatomic Molecules

XII. Some Planar Five-Membered Ring Structures

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Considerable interest is attached to heterocyclic five-membered ring structures, for which some modern spectroscopic and structural investigations have been completed, and further developments are in progress. In the present communication we wish to propose symmetry coordinates of molecular vibrations applicable to the four structures shown in Fig. 1. They are the (i) five-particle ring, which is the skeleton of all the here considered models, (ii) 1,3,4-thiadiazole,^{1,2} (iii) 1,2,5-thiadiazole,³ and (iv) thiophene⁴ or furan⁵ type molecular models.

The considered models all have the symmetry of C_{2v} . Fig. 1 shows the proposed numbering of atoms, which preserves consecutive numbering within each group of symmetrically equivalent atoms.

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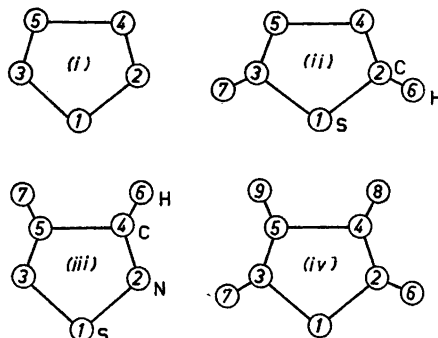


Fig. 1. Five-membered ring structures of C_{2v} symmetry.

It is not difficult to set up a complete set of symmetry coordinates without redundants in several different ways. We have chosen the alternative based on the valence coordinates explained on Fig. 2. Here the parenthesized symbols refer to out-of-plane coordinates: τ is used to denote ring torsions, while γ and ε denote out-of-plane bendings which involve the outer atoms.

Table 1 shows the actual symmetry coordinates. They are applicable to all the models (i, ii, iii, iv) shown in Fig. 1, when the appropriate expressions are selected according to the indication in Table 1.

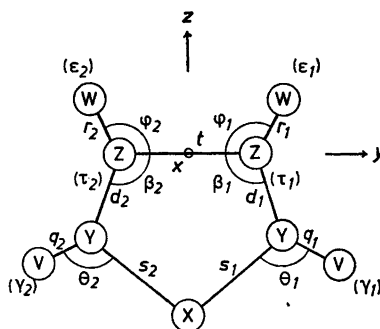


Fig. 2. The planar five-membered ring model $X(YV)_2(ZW)_2$; symmetry C_{2v} . Equilibrium parameters may conveniently be identified by corresponding capital letters. A sufficient set of equilibrium parameters is: $S, D, T, B, Q, \Theta, R, \Phi$.