960. *Out-of-plane Co-ordinates for the Vibrations of Planar Aromatic Molecules.*

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A comparison is made between the conventional valence-field-co-ordinate treatment of the out-of-plane motion of a planar aromatic molecule, and the use of another set of co-ordinates recently introduced by Coulson and Senent. It is shown that in the latter scheme interaction constants in the potential energy function are very much smaller than in the former and may therefore often be completely neglected. Equations are given that enable the equations of motion of such a molecule to be written down in a very convenient form and permit simple calculation of the displacements in sterically overcrowded molecules of this type.

When studying the out-of-plane vibrations of a planar aromatic molecule it is usual[1] to employ valence force co-ordinates (VFC). General methods have been given by Wilson[2] and Eliashevich[3] for setting up the secular determinant for these vibrations. An advantage of this theory is that the force constants have an explicit and simple physical meaning, and can often be transferred from one molecule to another. But recently, in the course of their study of certain overcrowded polynuclear hydrocarbons, Coulson and Senent[4] found it convenient to introduce another set of co-ordinates, which also have a simple physical meaning.

In order to compare the two sets of co-ordinates, let us consider (Fig. 1) part of a planar molecule to which the co-ordinates are applicable. The numbers 1 . . . 6 denote the atoms, and $\phi_1 \ldots \phi_6$ denote the angles. Since the bond lengths will not usually all be equal, we denote by a_{ik} the bond length between atoms i and k. Then the two sets of co-ordinates used to describe the out-of-plane behaviour of this atomic configuration are:

(1) the co-ordinates used, for example, by Miller and Crawford[5] in their calculations of the benzene molecule, and typified by:

γ_{13} = angle between the 1,3-bond and the plane 2–1–4
δ_{12} = torsion angle between the planes 2–1–4 and 1–2–6.

(2) the co-ordinates proposed by Coulson and Senent,[4] which, apart from certain scale factors, are equivalent to:

α'_1 = distance of atom 1 from the plane of its three neighbours 3–4–2.
β'_{12} = angle between the projections on to a plane perpendicular to 1–2 of two vectors, one of which is perpendicular to the plane 3–1–4 and the other to the plane 2–5–6.

We shall refer to these two sets of co-ordinates as MC and CS respectively. One advantage of the CS co-ordinates is that there is no ambiguity in their choice, such as is involved in δ_{12} where instead of the planes 2–1–4 and 1–2–6 we might have chosen 3–1–2 and 1–2–5. Another advantage seems to be that surprisingly good results can be obtained, both for spectral frequencies and structural equilibrium,[4,6,7] when only two force constants are used in the usual harmonic oscillator potential function, and with no cross-terms. Our objects in this paper are to understand the latter situation, and to provide a general

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[1] See, *e.g.*, Wilson, Decius, and Cross, " Molecular Vibrations," McGraw-Hill Book Co., New York, Toronto, London, 1955.
[2] Wilson, *J. Chem. Phys.*, 1939, **7**, 1047; 1941, **9**, 76.
[3] Eliashevich, *Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **28**, 605.
[4] Coulson and Senent, *J.*, 1955, 1813.
[5] Miller and Crawford, *J. Chem. Phys.*, 1946, **14**, 282.
[6] Coulson and Senent, *J.*, 1955, 1819.
[7] Ali and Coulson, *J.*, 1959, 1558.

method for setting up the potential function in terms of the displacements z_i of the atoms perpendicular to the mean plane.

Relations between the Sets of Co-ordinates.—In comparing the MC and CS co-ordinates it is convenient to use a relative reciprocal bond length A_{ik} rather than a_{ik}, where

$$A_{ik} = d/a_{ik} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In (1), d is the most characteristic bond length (1·39—1·40 Å for most aromatic compounds). Then straightforward trigonometric and analytical considerations lead to the following relations:

$$\alpha'_1 = \frac{A_{41}\sin\phi_4(z_4 - z_1) + A_{31}\sin\phi_3(z_3 - z_1) + A_{21}\sin\phi_2(z_2 - z_1)}{A_{41}\sin\phi_4 + A_{31}\sin\phi_3 + A_{21}\sin\phi_2} \quad . \quad . \quad . \quad . \quad (2)$$

$$\beta'_{12} = \frac{A_{31}\cos\phi_3(z_3 - z_1) - A_{41}\cos\phi_4(z_4 - z_1)}{d\sin\phi_2} - \frac{A_{52}\cos\phi_5(z_5 - z_2) - A_{62}\cos\phi_6(z_6 - z_2)}{d\sin\phi_1} \quad . \quad (3)$$

Usually $\phi_1 = \ldots = \phi_6 \approx 2\pi/3$; and then these equations are equivalent, apart from a scale factor, to those given by Coulson and Senent[4] and generalised by Ali and Coulson.[7]

FIG. 1.

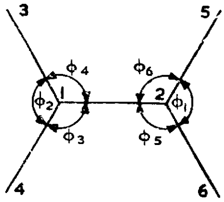
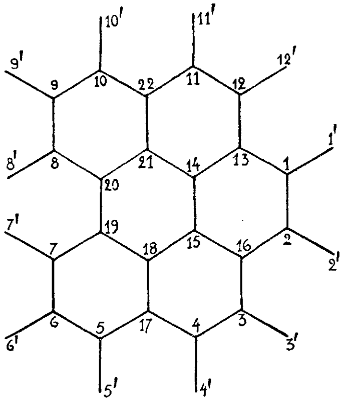


FIG. 2.



In what follows we shall discuss only this particular case, since, although generalisation to other cases is possible, the formulæ are rather complicated. It will now be convenient to take account of the scale factor, and replace α', β' by α, β as defined by Coulson and Senent. So from here onwards

$$\alpha_1 = A_{41}(z_4 - z_1) + A_{31}(z_3 - z_1) + A_{21}(z_2 - z_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\beta_{12} = A_{31}(z_3 - z_1) - A_{41}(z_4 - z_1) - A_{52}(z_5 - z_2) + A_{62}(z_6 - z_2) \quad . \quad (5)$$

We can also similarly find the relation between the MC co-ordinates and the Cartesian displacements z_i. When $\phi_1 = \ldots = 2\pi/3$, we have

$$\gamma_{13} = \frac{1}{d}\{A_{41}(z_4 - z_1) + A_{31}(z_3 - z_1) + A_{21}(z_2 - z_1)\} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\delta_{12} = \frac{2}{\sqrt{3}d}\{A_{62}(z_6 - z_2) - A_{41}(z_4 - z_1) - A_{21}(z_2 - z_1)\} \quad . \quad . \quad . \quad . \quad (7)$$

The lack of symmetry in the definition of δ_{12} is well brought out by equation (7).

By comparing (4)—(7) we see that

$$\gamma_{13} = \frac{1}{d}\alpha_1 \qquad (8)$$

$$\delta_{12} = \frac{1}{\sqrt{3}d}(\beta_{12} + \alpha_2 - \alpha_1) \qquad (9)$$

Comparison for Benzene.—We are now in a position to compare the MC and CS potential functions; and we shall choose benzene as our example, since the force constants in the MC scheme are already known [8] with good precision. If we limit ourselves to interaction terms of *ortho*-type only, we have in the MC representation:

$$\begin{aligned} V = {} & \tfrac{1}{2}A\sum(r\gamma_{\mathrm{i}})^2 + \tfrac{1}{2}B\sum(R\delta_{\mathrm{i,i+1}})^2 + a\sum r^2\gamma_{\mathrm{i}}\gamma_{\mathrm{i+1}} \\ & + b\sum R^2\delta_{\mathrm{i,i+1}}\delta_{\mathrm{i+1,i+2}} + c\sum rR(\gamma_{\mathrm{i}}\delta_{\mathrm{i-1,i}} - \gamma_{\mathrm{i}}\delta_{\mathrm{i,i+1}}) \qquad (10) \end{aligned}$$

where the bond lengths $r = 1{\cdot}08$ Å, $R = 1{\cdot}40$ Å are used for dimensional convenience, and γ_{i} is used instead of $\gamma_{\mathrm{i,k}}$, where k is the hydrogen atom adjacent to carbon atom i. In the CS representation

$$\begin{aligned} V = {} & \tfrac{1}{2}K^{\alpha}\sum\alpha^2_{\mathrm{i}} + \tfrac{1}{2}K^{\beta}\sum\beta^2_{\mathrm{i,i+1}} + K^{\alpha\beta o}\sum\beta_{\mathrm{i,i+1}}(\alpha_{\mathrm{i+1}} - \alpha_{\mathrm{i}}) \\ & + K^{\alpha o}\sum\alpha_{\mathrm{i}}\alpha_{\mathrm{i+1}} + K^{\beta o}\sum\beta_{\mathrm{i,i+1}}\beta_{\mathrm{i+1,i+2}} + K^{\alpha\beta m}\sum\beta_{\mathrm{i,i+1}}(\alpha_{\mathrm{i+2}} - \alpha_{\mathrm{i+1}}) \\ & + K^{\alpha m}\sum\alpha_{\mathrm{i}}\alpha_{\mathrm{i+2}} + \ldots \qquad (11) \end{aligned}$$

where the symbols *o* and *m* in the superscripts attached to the interaction constant *K* denote *ortho*- and *meta*-positions.

A comparison of equations (10) and (11), using (8) and (9), shows that if we use λ for the ratio $\lambda = R/r = 1{\cdot}2963$, then

$$\begin{aligned} K^{\alpha} &= \frac{1}{\lambda^2}A + \tfrac{2}{3}B - \tfrac{2}{3}b + \frac{4}{\lambda\sqrt{3}}c \\ K^{\beta} &= \tfrac{1}{3}B \\ K^{\alpha\beta o} &= \tfrac{1}{3}B - \tfrac{1}{3}b + \frac{1}{\lambda\sqrt{3}}c \\ K^{\alpha o} &= -\tfrac{1}{3}B + \frac{1}{\lambda^2}\alpha + \tfrac{2}{3}b - \frac{2}{\lambda\sqrt{3}}c \\ K^{\beta o} &= \tfrac{1}{3}b = K^{\alpha\beta m} = -K^{\alpha m} \qquad (12) \end{aligned}$$

and

$$\begin{aligned} A &= \lambda^2\{K^{\alpha} + 2K^{\beta} - 4K^{\alpha\beta o} - 2K^{\beta o}\} \\ B &= 3K^{\beta} \\ a &= \lambda^2\{-K^{\beta} + 2K^{\alpha\beta o} + K^{\alpha o} + 2K^{\beta o} - 2K^{\alpha\beta m}\} \\ b &= 3K^{\beta o} \\ c &= -\lambda\sqrt{3}\{K^{\beta} - K^{\alpha\beta o} - K^{\beta o}\} \qquad (13) \end{aligned}$$

with the condition for zero *meta*-interactions

$$K^{\alpha\beta m} = K^{\beta o} = -K^{\alpha m} \qquad (14)$$

If we use the force constants $A, \ldots$ calculated in the MC scheme by Kakiuti and Shimanouchi [8] to compute the force constants $K^{\alpha}, \ldots$ we obtain the results shown in Table 1, in which the third and the sixth column give the value of the force constant as a percentage of the largest one (A and K^{α} respectively).

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[8] Kakiuti and Shimanouchi, *J. Chem. Phys.*, 1956, **25**, 1252.

TABLE 1. *Numerical values of the force constants.*

Force constants calculated by Kakiuti and Shimanouchi [8] *			Force constants in the considered VFC representation calc. from eqn. (12)		
Symbol	Value (10^5 dyne/cm.)	%	Symbol	Value (10^5 dyne/cm.)	%
A	0·402	100	K^{α}	0·1345	100
B	0·181	45·0	K^{β}	0·0603	44·8
a	−0·073	18·2	$K^{\alpha\beta o}$	0·0059	4·4
b	−0·012	3·0	$K^{\alpha o}$	0·0050	3·7
c	−0·131	32·6	$K^{\beta o}$	−0·0040	3·0

* Taking $r_0 = 1{\cdot}08$ Å, $R_0 = 1{\cdot}40$ Å

It is surprising how much the interaction constants given in the last three lines of this Table are reduced in the new CS co-ordinates. Thus the maximum value of an interaction constant is reduced from 32·6% in the MC scheme to 4·4% in the CS scheme. This explains why Coulson and Senent [4,6] and Ali and Coulson [7] obtained such good results even though they neglected all interaction constants. Incidentally the values which we obtain in Table 1 for K^{α} and K^{β} differ only slightly from those previously used by Coulson and Senent,[4] namely:

$$K^{\alpha} = 0{\cdot}1474 \times 10^5 \text{ dyne cm.}^{-1}; \quad K^{\beta} = 0{\cdot}0553 \times 10^5 \text{ dyne cm.}^{-1} \quad . \quad . \quad (15)$$

Since the calculation of interaction constants is the most troublesome part of the estimation of potential functions, and since according to equation (13) the influence of each separate K-force constant is additive in the determination of the A,B, . . . force constants, we show in Table 2 the way in which the K-interaction constants influence the MC constants A . . . c. In each column there are given the values of these constants when account is taken only of the CS constants listed at the head of the column. It can be seen from this Table that, at least in benzene, $K^{\alpha\beta o}$ is the most important interaction force constant, and $K^{\beta o}$ the least important in influencing A,B, . . . c.

TABLE 2. *The importance of the interaction terms of K type in determining the MC force constants.*

	K^{α},K^{β} from eqn. (15)	K^{α},K^{β}	K^{α},K^{β},$K^{\alpha o}$	K^{α},K^{β},$K^{\alpha\beta o}$	K^{α},K^{β},$K^{\beta o}$	K^{α},K^{β},$K^{\alpha o}$,$K^{\alpha\beta o}$,$K^{\alpha o}$	Exact value
A	0·433	0·429	0·429	0·389	0·442	0·402	0·402
B	0·166	0·181	0·181	0·181	0·181	0·181	0·181
a	−0·093	−0·101	−0·093	−0·081	−0·114	−0·086	−0·073
b	0	0	0	0	−0·012	−0·012	−0·012
c	−0·068	−0·135	−0·135	−0·122	−0·144	−0·131	−0·131

(and small values for the *meta*-interaction terms in the MC representation.)

APPENDIX

In all applications of the CS co-ordinates to the out-of-plane deformations of overcrowded molecules, or to the calculation of out-of-plane normal modes of vibration, it is necessary to form the expressions

$$\frac{1}{K_{\alpha}}\frac{\partial V}{\partial z_{\mathrm{i}}} = \sum_{k} u_{\mathrm{ik}} z_{\mathrm{k}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

for all i's. The coefficients u_{ik} are simple to obtain from an expression such as (11), but it is very tedious when dealing with large molecules. We have therefore set down in Table 3 a general formula for u_{ik}. For the sake of definiteness we first list the assumptions under which this Table is valid.

(i) All the bond angles are 120°, and all the carbon–carbon bond lengths have $A_{\mathrm{ik}} = 1$.

(ii) Each carbon atom is in the sp^2-state of hybridisation, and no such carbon atom has more than one non-carbon neighbour (this is usually hydrogen).

(iii) The potential energy is a quadratic form of the co-ordinates (4)—(5), and all interaction force constants are neglected. We have seen that these interaction constants are small; they may, of course, be added if we so desire; but then the formulæ of Table 3 become considerably more complicated.

The following definitions will be used:

s = general carbon or hydrogen atom, with respect to which the potential energy is being differentiated to give $\partial V/\partial z_s$,
o = a nearest neighbour atom to s (*ortho*),
m = a second nearest neighbour atom to s (*meta*),
p = a third nearest neighbour atom to s (*e.g.*, *para*),
x = hydrogen neighbour atom of s (if any),
y = hydrogen neighbour atom of m (if any),
z = hydrogen neighbour atom of p (if any),
$n_{ab\ldots}^{cd\ldots}$ = the number of torsion axes passing through a,b . . . and not through c,d, . . .,
$N_{ks}^{lm} = +n_{ks}^{lm}$ when l and m refer to atoms on the same side of the axis ks,
$= -n_{ks}^{lm}$ when l and m refer to atoms on different sides of the axis ks,
$\mathscr{N}_{sp}$ = number of shortest paths, from atom s to atom p along the bonds (this must be either 1 or 2),
$\lambda = 1{\cdot}40/1{\cdot}08$ (Å) $= 1{\cdot}2963$,
$\Lambda = K^{\beta}/K^{\alpha} = 0{\cdot}4483$

TABLE 3. *Formulæ for the coefficients* $u_{is} \equiv u_{si}$.

s i	s(H) (a hydrogen atom)	s(C_s) (a secondary carbon atom)	s(C_t) (a tertiary carbon atom)
s(H)	$(1 + 2\Lambda)\lambda^2$	—	—
s(C_s)	—	$(2 + \lambda)^2 + 2 + \{2\lambda^2 - 4\lambda + 2 + \sum_o n_o^s\}\Lambda$	—
s(C_t)	—	—	$12 + \Lambda\sum_o n_o^s$
o(C_s)	$-(2 + \lambda)\lambda + 2\Lambda(1 - \lambda)\lambda$	$-(4 + 2\lambda) + \Lambda(\lambda - 1)[2 - (\lambda - 1)N_{os}^{xy}]$	$-(5 + \lambda) + (\lambda - 1)\Lambda$
o(C_t)	—	$-(5 + \lambda) + (\lambda - 1)\Lambda$	-6
m(C_s)	$\lambda\{1 + \Lambda[(\lambda - 1)N_{om}^{sz} - 1]\}$	$1 + \{(\lambda - 1)(N_{om}^{sz} + N_{os}^{mx}) - n_o^{sm}\}\Lambda$	$1 + \{(\lambda - 1)N_{om}^{sz} - n_o^{sm}\}\Lambda$
m(C_t)	$(1 - \Lambda)\lambda$	$1 + \{(\lambda - 1)N_{os}^{mx} - n_o^{sm}\}\Lambda$	$1 - n_o^{sm}\Lambda$
p(C_s) p(C_t)	$-\Lambda N_{om}^{sp}\lambda$	$-\mathscr{N}_{sp}\Lambda N_{om}^{sp}$	$-\mathscr{N}_{sp}\Lambda N_{om}^{sp}$
p(H)	$-\Lambda N_{om}^{sp}\lambda^2$	$-\Lambda N_{om}^{sp}\lambda$	$-\Lambda N_{om}^{sp}\lambda$

(Note: The first main column gives u_{is} when s is a hydrogen atom, the second when s is a secondary carbon atom, and the third when s is a tertiary carbon atom. Also, o, m in N_{om}^{sp} refer to those atoms in *ortho*- and *meta*-position, which are between the atoms s and p. Similarly o in N_{om}^{sz} and N_{os}^{mx} refers to that atom in the *ortho*-position to s, which lies between the atoms s and m).

Let us illustrate the use of this Table by taking as an example the calculation of $\partial V/\partial z_1$ in 1,12-benzoperylene (Fig. 2). The molecular diagram shows that $n_{1'}^1 = 0$, $n_2^1 = 1$, $n_{13}^1 = 2$, index s = 1 referring to a secondary carbon atom. Hence

$$u_{1,1} = (2 + \lambda)^2 + 2 + (2\lambda^2 - 4\lambda + 5)\Lambda$$

Similarly:

$u_{1,13} = -(5 + \lambda) + (\lambda - 1)\Lambda$
$u_{1,14} = 1 - \lambda\Lambda$, since $N_{os}^{mx} = N_{13,1}^{14,1'} = -1$ and $n_o^{sm} = n_{13}^{1,14} = 1$,
$u_{1,15} = -2\Lambda$, since $N_{om}^{sp} = N_{2,16}^{1,15} = N_{13,14}^{1,15} = 1$, and so on.

One of us (A. G.) acknowledges the award of a Rockefeller Foundation Fellowship, and leave of absence (1959—1960) from the Department of Theoretical Chemistry of the Jagellonian University of Cracow.

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[*Received, June* 16*th*, 1960.]