104. *The Mechanism of Additions to Double Bonds. Part III. Molecular Forces between Benzoquinone and* cyclo*Pentadiene.*

By Albert Wassermann.

London has given the following approximation formula for the attraction energy for simple molecules due to the " dispersion effect " (*Z. Physik*, 1930, **63**, 243; *Z. physikal. Chem.*, 1930, **11**, *B*, 222):

$$\varepsilon_{kl} = \frac{3}{2} \times \frac{P_k P_l}{R^6} \frac{\Delta E_k \times \Delta E_l}{\Delta E_k + \Delta E_l} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where R is the distance between the molecules k and l. The polarisability P of these molecules at the frequency ν is given by

$$P_k(\nu) = \frac{1}{m}\left(\frac{eh}{2\pi}\right)^2 \sum_{k'} \frac{f_{kk'}}{(E_{k'} - E_k)^2 - h^2\nu^2}$$

and similarly for $P_l(\nu)$; here m is the mass of the electron and $f_{kk'}$ the oscillator strength (" number of dispersion electrons ") corresponding to the eigenfrequency $(E_{k'} - E_k)/h$.

The energy difference corresponding to the greatest f value is termed ΔE_k. In this communication an attempt is made to extend the use of formula (1) to the calculation of energies between large organic molecules. Such an attempt is not in contradiction with the assumptions under which formula (1) has been deduced. The attraction between each bond in k and each bond in l is separately calculated and then added together to give the total dispersion effect, additivity being a characteristic property of these molecular forces. The approximately constant bond refractivities, which, it is known, can be ascribed to the various bonds in organic molecules (cf. Smyth, *Phil. Mag.*, 1925, **50**, 301; Fajans and Knorr, *Ber.*, 1926, **59**, 245), can be used for the calculation of P in formula (1). The polarisabilities here involved have been regarded as isotropic spheres located in a point in the middle of each bond (cf. also p. 435); R in (1) is the distance between these points in k and l respectively. It has been observed in many cases that some bonds (*e.g.*, conjugated double bonds) have not only a characteristic refractivity but also a characteristic absorption from which ΔE_k and ΔE_l can be estimated. As no absorption bands of C—C or C—H bonds are known,* the ionisation energy of carbon (11 e.v.) has been used for ΔE_{C-C}, and half the sum of the ionisation energy of carbon and hydrogen (12 e.v.) for ΔE_{C-H}.†

If the application of formula (1) is permissible in the case of large molecules, and if the order of magnitude of the ΔE values has been correctly estimated, then the calculated lattice energy of organic crystals should be of the same order of magnitude as the experimentally determined heat of sublimation. This has been proved to be true for the case of benzoquinone (see Section 1). In Parts I and II (J., 1935, 828, 1511) the dipole induction energies for different mutual orientations of benzoquinone and *cyclo*pentadiene were calculated, and it was shown that, under certain assumptions, the difference in the induction energies was sufficient to explain the actual course of the additive reaction. One of the assumptions concerns the magnitude of the dispersion effect. In Section 2, values of this dispersion effect are calculated and compared with the dipole induction energies.

1. *The Lattice Energy of Benzoquinone.*—The mutual orientation of the molecules in the benzoquinone crystal is known (Robertson, *Proc. Roy. Soc.*, 1935, **150**, 106). For the C—H distance the value (*viz.*, 1·1 Å.) given in Part I (Figs. 2—4) was used. The P and ΔE values are given below.

Bond	C═C (Benzoquinone).	C═O (Benzoquinone).	C—C.	C—H.
$P \times 10^{24}$ (cm.^{3})	1·87	1·58	0·478	0·671
ΔE (e.v.)	5·2	5·2	11	12

The " non-localised " electrons in the conjugated double bonds of benzoquinone produce a certain exaltation of the molecular refractivity (cf. von Auwers, *Ber.*, 1927, **60**, 2143); this exaltation was regarded as being equally distributed between the four double bonds. The refraction of the C═C bond is then 4·75, and that of the C═O bond 4·02; from these figures the P values quoted above were calculated. The ΔE value for the C═C and the C═O bond was deduced from an absorption band at 2400 Å. in benzoquinone vapour ‡ (Light, *Z. physikal. Chem.*, 1926, **122**, 414). That this band does really correspond to an excitation of electrons of the conjugated double bonds is rendered very probable by a comparison with the absorption spectra of the polyenes (cf. Hausser, Kuhn, *et al.*, *Z. physikal. Chem.*, 1935, **29**, *B*, 363). The observed regular displacement of the position and intensities of the bands of the polyenes as the number of double bonds is increased indicates that the electrons of conjugated double bonds are so closely coupled that for many purposes they can be treated collectively. It is therefore also justifiable to attach only one ΔE

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* The deduction of ΔE values for C—C and C—H bonds from magnetic susceptibilities is possible (private communications from Dr. Eisenschitz and Dr. Muller; cf. a paper in *Proc. Roy. Soc.* in press).

† The same ΔE values have been used by Muller in calculating the heats of sublimation of some aliphatic hydrocarbons (preliminary communication in " The Solid State of Matter," International Congress of Physics, 1934, **2**, 52). The second ionisation potential of benzene is 11·7 ± 0·3 e.v. (Price and Wood, *J. Chem. Physics*, 1935, **3**, 439). This value is almost the same as that used for ΔE_{C-H}.

‡ This band is also shown by solutions; its f value is about 1000 times as great as that of the band to which the yellow colour of quinone is due.

value to each system of conjugated double bonds of other compounds, *e.g.*, benzoquinone or *cyclo*pentadiene. These values are, of course, considerably smaller than the minimum ΔE value of ethylene (for the absorption of ethylene, cf. Scheibe and Grieneisen, *Z. physikal. Chem.*, 1934, **25**, *B*, 52).

The figure shows a part of the benzoquinone lattice. The energy between molecule 1 and a number of other molecules is given in Table I.

TABLE I.

Energies (*ergs* × 10^{14}) *between various molecules in the benzoquinone lattice.*

Molecules (see fig.)	1—2	1—3	1—4	1—5	1—6	1—7
Dispersion effect	−15	− 4	− 1·0	− 5·7	− 1·8	− 5·0
Dipole-induction energy	− 6	− 1·3	− 0·5	− 1·4	− 0·2	− 2·0
Dipole energy	− 9	− 8·6	− 1·0	+ 1·2	− 2·4	+ 9·6
Sum	−30	−13·9	− 2·5	− 5·9	− 4·4	+ 2·6

Calculation of the dispersion effect between the nearest C═C bonds of the molecules 1 and 2 gives

$$\varepsilon_{C=C(1),\, C=C(2)} = \frac{3 \times (1{\cdot}87 \times 10^{-24})^2 \times 5{\cdot}2^2 \times 4{\cdot}77 \times 10^{-10}}{2 \times R^6 (5{\cdot}2 + 5{\cdot}2) \times 300} \text{ erg}$$

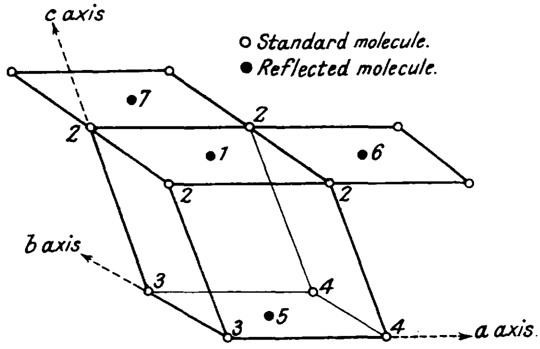
The distance R is 3·9 Å. (cf., *e.g.*, Fig. 4 in Robertson's paper). Each dispersion effect of Table I is the sum of 144 similarly calculated energies.

The dipole-induction energy was calculated as in Part I (*loc. cit.*). The dipole energy equals μF. F is the electric intensity (for calculation, see Part I) due to the two dipoles of k at the points at which one of the dipoles of l is regarded as localised; μ is the component of this dipole in the direction of F.

The lattice energy is obtained from the data of Table I as follows :

$$\tfrac{1}{2} \times 6{\cdot}06 \times 10^{23} \times 0{\cdot}239 \times 10^{-7} \times 10^{-14} \times 10^{-3} \times$$
$$[4 \times 30 + 4 \times 13{\cdot}9 + 4 \times 2{\cdot}5 + 2 \times 5{\cdot}9 + 2 \times 4{\cdot}4 - 2 \times 2{\cdot}6]$$
$$= 14{\cdot}6 \text{ kg.-cals./mol.} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

The energy between molecule 1 and those molecules of the lattice which have not been included in the summation is only a few units per cent. of the total energy, and can be neglected.



Part of the benzoquinone lattice. The circles indicate the position of the centre of symmetry of the molecules. The mutual orientation of the molecules is shown in Robertson's paper (loc. cit.).

If the energy (2) is to be compared with the experimental heat of sublimation of benzoquinone, the kinetic energy of the crystal and the repulsive forces between the molecules should be taken into account. As a first approximation it seems justifiable to neglect these two terms (the repulsive forces were also neglected in London's calculation of lattice energies, *loc. cit.*) ; then the lattice energy, as calculated by (2), and the heat of sublimation should roughly coincide. This is the case, for the heat of sublimation (determined between − 7° and + 5° by Coolidge and Coolidge, *J. Amer. Chem. Soc.*, 1927, **49**, 105) is 15 kg.-cals./mol.* It can therefore be concluded that application of formula (1) is permissible, and that the order of magnitude of the ΔE values has been correctly estimated. If, as a second approximation, the repulsive forces are considered, then it is obvious that the calculated potential energy should be larger than 15 kg.-cals. As this was not found to be the case, it is probable that certain ΔE values are too small. The ΔE's of the double bonds were deduced from

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* Such close agreement with the calculated figure is, of course, fortuitous.

experimentally observed absorption bands. On the other hand, the values of $\Delta E_{\mathrm{C-C}}$ and $\Delta E_{\mathrm{C-H}}$ were arbitrarily chosen, and it is therefore probable that these values are larger than 11 and 12 volts respectively.

A calculation of the lattice energy of benzoquinone, based only on the attraction due to the dipole and dipole-induction energy (cols. 3 and 4 of Table I) would give a value of 7 kg.-cals./mol. In spite of the fact that benzoquinone contains both the strongly polar C=O group and strongly polarisable double bonds, the classical dipole and dipole-induction energy does not amount to more than about 50%, at the most, of the total attraction.

2. *Dispersion Effect between Benzoquinone and* cyclo*Pentadiene.*—For the calculation of the data in Table III, the bond refractivities of *cyclo*pentadiene, as given in Part I, were used.* For the C=C bonds in *cyclo*pentadiene, a ΔE value of 6·2 e.v. was taken, corresponding to an absorption band in gaseous *cyclo*pentadiene at about 2000 Å. (Scheibe and Grieneisen, *loc. cit.*). Ethane absorbs continuously down to λ 1590 Å. It follows that in ethane, and certainly also in other molecules, $\Delta E_{\mathrm{C-C}}$ and $\Delta E_{\mathrm{C-H}}$ must be larger than 8 e.v.† Hence for $\Delta E_{\mathrm{C-C}}$ and $\Delta E_{\mathrm{C-H}}$, not only the values taken before, but also a value of 8 e.v. was used. Those figures in Table III given in parentheses were calculated on the assumption that $P_{\mathrm{C-H}}$ is localised, not in the middle of each bond, but at a distance of 0·4 Å. from the centre of the carbon atom.

The mutual orientations of benzoquinone and *cyclo*pentadiene referred to are shown in Figs. 2—4 of Part I. The atomic distance d characterising the degree of separation of the two molecules is defined in the same way as before. From the data in Table II it can be seen that the closest packing between the carbon atoms of *cyclo*pentadiene and the carbon and oxygen atoms of benzoquinone corresponds to the intermediate configuration leading to the *endo*-1 : 4-addition product.

TABLE II.

Distance between carbon and oxygen atoms in different mutual orientations (intermediate configurations) of benzoquinone and cyclo*pentadiene.*

(Distance d arbitrarily chosen as 2·33 Å.)

		Intermediate configuration suitable for		
	a.	1 : 2-addition (cf. Fig. 4, Part I).	*exo*-1 : 4-addition (cf. Fig. 3, Parts I and II).	*endo*-1 : 4-addition (cf. Fig. 2, Parts I and II).
Number of carbon atoms of *cyclo*pentadiene which are at a distance of not more than *a* Å. from carbon atoms of benzoquinone	2·33	2	2	2
	2·4	2	2	4
	2·5	2	3	5
Number of carbon atoms of *cyclo*pentadiene which are at a distance of not more than β Å. from oxygen atoms of benzoquinone	β.			
	3·1	0	2	4
	3·5	2	3	4

As formula (1) is valid only when P/R^3 is considerably smaller than unity, the dispersion effect—in contrast to the dipole-induction energies as given in Parts I and II—cannot be calculated for d values smaller than about 2·33 Å. For $d = 2{\cdot}33$ Å., $P/R^3 = 0{\cdot}13$ at the most.

TABLE III.

Attraction energy (due to dispersion effect) between benzoquinone and cyclo*pentadiene in kg.-cals./mol.; d = 2·33 Å.*

$\Delta E_{\mathrm{C-C}}$ and $\Delta E_{\mathrm{C-H}}$, e.v., used for calcn. of dispersion effect.	Intermediate configuration suitable for		
	1 : 2-addition.	*exo*-1 : 4-addition.	*endo*-1 : 4-addition.
8	−16·1	−21·9	−25·1
11 and 12...	−19·0	−24·9 (−24·0)	−29·2 (−30·0)

1 : 2- *and* endo-1 : 4-*Addition.* The values in cols. 2 and 4 of Table III show that the dispersion effect is greater by 9—10 kg.-cals. when the molecules take up the orientation

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* The fact that the calculated molecular refractivity of *cyclo*pentadiene is a little higher than the observed value (von Auwers, *Ber.*, 1912, **45**, 3077) was not taken into account.

† This conclusion is independent of the consideration discussed on p. 434.

suitable for *endo*-1 : 4-addition. Moreover, for this orientation, in which the carbon and oxygen atoms of the reacting molecules are more closely packed, the dipole-induction energy was found to be larger.

exo- *and* endo-*Addition.* In view of the closer packing of the carbon and oxygen atoms in the "*endo*-intermediate configuration," it would be expected *a priori* that here the dispersion effect would be larger. From the data in cols. 3 and 4 it can be seen that the difference of the dispersion effects is only 3—6 kg.-cals. It might seem dangerous to draw conclusions from a difference which is so small compared with the quantities involved, but it is evident that the difference increases as the values assumed for ΔE_{C-C} or ΔE_{C-H} are increased. As the real ΔE values may be even greater than 11 or 12 e.v. (cf. p. 434), it can be concluded that the dispersion effect corresponding to the "*exo*-intermediate configuration" is not greater than that corresponding to the "*endo*-intermediate configuration." The difference in the total-attraction energy (sum of dispersion effect and dipole-induction energy) is therefore not less than the difference in the dipole-induction energy.

SUMMARY.

London has deduced an approximation formula for the attraction energy for simple molecules, due to the dispersion effect. An attempt is made to extend the use of this formula to the calculation of energies between large organic molecules. In order to test the method the lattice energy of benzoquinone has been calculated. The agreement with the experimental heat of sublimation is satisfactory. For an understanding of the course of diene syntheses (*e.g.*, addition of benzoquinone to *cyclo*pentadiene) it is important to estimate the attraction energies of the reacting molecules in different mutual orientations. The attraction energy due to the dispersion effect between benzoquinone and *cyclo*pentadiene is calculated for three orientations and is compared with the dipole-induction energies.

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