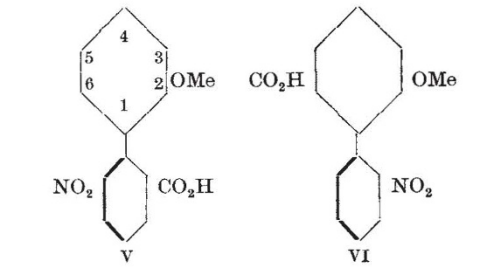
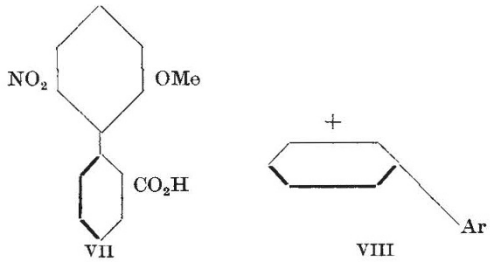
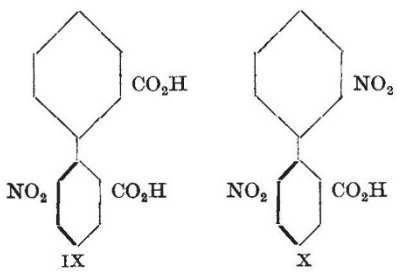




Apparently, the sizes of the substituents are not the sole determining factor of the rates of racemization.

Fischer models of these diphenyl derivatives show that the rotation required for racemization encounters much less obstruction when the bond joining the two rings is displaced from the plane of one of them by the introduction of a tetrahedral carbon atom. The displacement is shown in VIII, and its occurrence must depend on the ability of the carbon atom at which it occurs to acquire a negative charge, for the configuration is that of a negatively charged carbon atom. If such a displacement plays a part in facilitating racemization, this displacement will occur in the ring of greater electron density, and the rate of racemization will be related to the electron density in this ring.

Data from various sources have shown that the nitro group exceeds the carboxyl group in decreasing the electron density of an aromatic ring to which these groups are attached, whereas the methyl and methoxyl groups have the opposite effect. On the assumption that the effect of the carboxyl group lowers the electron density to a greater extent than does the combined effect of the nitro and methyl groups or the nitro and methoxyl groups, each of the diphenyls II–VII has been written with the ring of greater electron density uppermost. Comparing these upper aromatic rings with one another, the electron densities are in the order II > III > IV and V > VI > VII, which is also the order of the rates of racemization. This connexion between electron density and rate of racemization is strengthened by the influence of various substituents on the optical stability of V[3]. In general, the more 'negative' the substituent in the *upper* ring, that is, the lower the electron density in this ring, the greater the optical stability. Thus, the 4-nitro derivative is more stable and the 4-methyl derivative less stable than V. These substituents have a smaller effect on the stability when attached at the 5-position; here, they have a smaller effect on the electron density at the 1-position.



Finally, the racemization of IX and X should be related to the electron densities in the upper aromatic rings, since these contain only one 'negative' substituent; comparing these upper rings, only that in IX undergoes a considerable increase of electron density when the acids are converted into the corresponding anions by the addition of alkali. The accompanying table shows that the addition of alkali greatly decreases the optical stability of IX but not that of X.

Solvent	Half-life period (min.) IX	X
CH_3CO_2H	91·9	125·1
n—C_4H_9OH	101·1	91·9
NaOH(0·1 *N*)	4·6	91

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[1] Adams and Hale, *J. Amer. Chem. Soc.*, **61**, 2825 (1939).
[2] Adams and Finger, *J. Amer. Chem. Soc.*, **61**, 2828 (1939).
[3] Handford and Adams, *J. Amer. Chem. Soc.*, **57**, 1592 (1935).

Cyclo-octatetraene

RECENT work by Reppe[1] has proved that Willstätter's hydrocarbon C_8H_8 has indeed the cyclo-octatetraene structure which was originally assigned to it. Its reactions enabled him to conclude that "the double bonds of cyclo-octatetraene are open to all the reactions of ethylenic chemistry". This conclusion might at first sight be taken to indicate the absence of resonance in this molecule. However, this would be in contradiction to the physical data on the heat of combustion and the absorption of light, which can be taken as indicative of a resonating molecule. The heat of combustion leads to a value of 28 kcal. for the resonance energy, compared with 41 kcal. for benzene. The substance is described as a golden yellow liquid, which places the long wave-length ultra-violet system corresponding to the 2600 A. band of benzene at about 4000 A. If it contained fixed double bonds, then the absorption would be expected to lie below 2000 A. Thus the evidence from the heat of combustion and the absorption spectrum indicates a resonating molecule.

Penney[2] and Wheland[3] have studied the quantum mechanics of a planar, non-strained ring of eight CH-groups by the valence bond method. The predicted ratio of the resonance energy of this model to the resonance energy of benzene is 1·17. Accepting this model, it would not appear unreasonable to attribute the difference between the calculated and observed resonance energies, that is, (1·17 × 41–28) kcal. or 20 kcal. to strain. Forster[4] has shown that resonance between the two Kekulé forms should lead to a maximum of absorption at 4100 A., in good agreement with experiment. As neglect of the excited structures of the canonical set leads to a very poor approximation to the resonance energy, it was thought desirable to carry out a calculation of the light absorption using the complete set of fourteen structures. A preliminary treatment neglecting the second excited structures leads to a value of 3550 A. for the maximum of the long wave-length ultra-violet system. The inclusion of the four second excited structures does not alter this value appreciably. The fact that the calculated absorption maximum lies at a shorter wave-length than the observed would be consistent with a strained molecule.

If the resonance energy and the light absorption of a strained molecule are known, then it is possible to estimate the strain in both the ground and excited states. If, as might be expected, the strain is reduced in the excited state, then the molecule should absorb at a longer wave-length than that calculated with the neglect of strain.

Another interpretation of the low value of the resonance energy is that the ring is puckered. The strain in the ring would thus be reduced at the expense of the resonance energy. At this stage it would be difficult to decide between the two possibilities.

It now remains to reconcile the chemical behaviour of the molecule with its resonance. In the first place, its resonance energy is of the order of that calculated by Kovner[5] for octatetraene (24 kcal.). Hence it would be expected to behave rather as a conjugated system than as an aromatic one. Again, the reactivity of cyclo-octatetraene may be due to the formation of a stable transition state[6]. It is of interest to note in this connexion that cyclo-octatetraene, like open-chain polyenes, is capable of reacting with benzoquinone and maleic anhydride, its reactions in these cases being typical diene syntheses. The question of the reactivity of cyclo-octatetraene would need further investigation, but it would appear that the chemical evidence is not necessarily in conflict with the physical and theoretical.

It is hoped to publish these results in more detail later, when the resonance energies and light absorption of a number of non-benzenoid aromatic hydrocarbons have been investigated.

I wish to express my gratitude to Dr. A. Wassermann for discussion on this topic.

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April 13.

[1] Report on Cyclopolyolefins, W. Reppe (Chem. Soc. Library, 1944).
[2] *Proc. Roy. Soc.*, A, **146**, 223 (1934).
[3] *J. Chem. Phys.*, **3**, 230 (1935).
[4] *Z. Elect.*, **45**, 548 (1939).
[5] *Acta Physicochimica U.R.S.S.*, **19**, 385 (1944). See also Pauling and Sherman, *J. Chem. Phys.*, **1**, 679 (1933), in which the value 30 kcal. is obtained.
[6] Evans, *Trans. Faraday Soc.*, **35**, 824 (1939).

Secondary Electron Photography

IN a letter in *Nature* (**156**, 150; 1945), Messrs. Tasker and Towers describe a method for the radiography of thin objects such as paper and fabrics, using secondary electrons emitted from a sheet of lead irradiated by high-voltage X-rays. Reference is made to complications which sometimes arise owing to the emission of electrons from the material radiographed, in the worst cases a partially positive picture appearing.

During the course of an examination of this method of radiography, a striking demonstration of the emission of photo-electrons from heavy elements has been observed. Some of the test objects used were postage stamps kindly loaned by Mr. W. H. S. Cheavin. Radiography by means of 10 kV. grenz rays showed that many such stamps were printed with inks containing a metallic base, and give a remarkably well-defined radiographic negative.

When these stamps were examined by the method of Tasker and Towers, a rather poor positive image was obtained. This suggested a further step, namely, the removal of the emitting lead sheet, and the direct radiography of the specimen with high-voltage radiation. The result was a positive image produced by the secondary electrons from the ink, and equal in quality to the grenz-ray radiograph. We therefore have the somewhat surprising result of two 'radiographs' of the same object, taken under almost identical conditions, the picture with 10 kV. radiation being negative, and with 190 kV. positive. A typical example of this phenomenon is shown in the accompanying photographs. To avoid confusion, both radiographs were taken