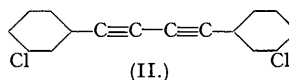
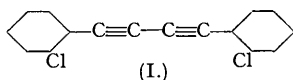


NOTE.

The Dipole Moments of Two Dichlorodiphenyldiacetylenes. By G. E. COATES.

THE single bonds in conjugated systems are generally shorter than those present in normal molecules; this is considered to be due to resonance effects which impart some double-bond character to the single bonds. In diphenylacetylene, for example, the "order" of the single bonds of the acetylene group is 1.48 (Robertson and Woodward, *Proc. Roy. Soc.*, 1938, *A*, **164**, 436; Penney and Kynch, *ibid.* p. 409). Partial double bonds of this type are known to impede free rotation and, conversely, the bond order appears to decrease when the molecular configuration is unfavourable to a high degree of conjugation (these effects are evident in the two forms of azobenzene discussed by Robertson, *Ann. Reports*, 1939, **36**, 175—185).

A particularly high degree of conjugation would be expected in the diphenyldiacetylene molecule, since Pauling, Springall, and Palmer (*J. Amer. Chem. Soc.*, 1939, **61**, 927) estimate that the central single bond in diacetylene has 44% double-bond character. In such highly conjugated systems the interesting possibility occurs that the degree of double-bond character present in the single bonds might be sufficient to prevent free rotation and allow *cis-trans* isomerism of suitable derivatives. The two substances 2 : 2'-dichlorodiphenyldiacetylene (I) and 3 : 3'-dichlorodiphenyldiacetylene



(II) have been prepared, but attempts to separate isomers have failed. It appears that the conjugation is not sufficient to prevent free rotation.

The dipole moments of (I) and (II), measured at 25° in benzene solution, are 1.92 and 1.91 D, respectively. The approximate equality of the moments indicates that the interaction between the chlorine substituent and the side chain is negligible, since any such interaction would undoubtedly affect the *ortho* much more than the *meta* compound. The

bond moments were therefore taken to be the same as in chlorobenzene, *viz.*, 1.56 D. (*Trans. Faraday Soc.*, 1934, **30**, Appendix: "A Table of Dipole Moments"). A moment of $1.56\sqrt{2} \cos 30^\circ = 1.91$ D. would be expected for both compounds if there were either complete freedom of rotation or complete locking with equal amounts of *cis* and *trans* isomers. Partially restricted rotation would give other values for the moment. Since the main body of the substances melted sharply after very few crystallisations, and since no isomers could be isolated from the mother liquors, the measured moments indicate freedom of rotation.

Dipole moments were measured by means of the apparatus and procedure described by Sutton (*Proc. Roy. Soc.*, 1931, *A*, **133**, 668). Measurement of refractive indices in dilute benzene solution at 5461 Å. indicated optical exaltations of 16.6 and 15.2 c.c. for the *o*- and *m*-compounds. There is undoubtedly an absorption band in the near ultra-violet, hence the electron polarisations (for the low frequency at which the dielectric constants were measured) could not be calculated from the measured refractivities; in such instances electron polarisations must be calculated from tables of atomic and bond refractivities, and extrapolated to infinite wave-length. This was the procedure adopted, since previous experience (Coates and Sutton, *J.*, 1942, 567) had shown that electron polarisations calculated from tables (Landolt-Börnstein, 5th Edition, 1923, Hauptwerk II, p. 985) agreed well with those calculated from measured refractivities. Atom polarisations were taken as 5% of the electron polarisations. Total polarisations were 154.0 and 153.1 c.c.; from the calculated orientation polarisations, 76.4 and 75.5 c.c., the moments were 1.92 and 1.91 D. respectively. Moments were not corrected for solvent effects.

2: 2'-Dichlorodiphenyldiacetylene. The sparingly soluble cupric salt of *o*-chlorophenylpropionic acid (Bergmann and Bondi, *Ber.*, 1933, **66**, 282) was prepared by the addition of a solution of the sodium salt to a slight excess of aqueous cupric chloride. The dry cupric salt (45 g.) was warmed with pyridine (150 c.c.) on a water-bath for $\frac{3}{4}$ hour; carbon dioxide was evolved. Benzene (200 c.c.) was added to the cooled and filtered solution, and the pyridine removed with hydrochloric acid. The residue from evaporation of the dried benzene solution was boiled with charcoal in ethyl alcohol and crystallised four times from ethyl alcohol; final yield of the *compound*, 8 g. of feathery crystals, m. p. 139.5—140.0° (corr.) (Found: C, 70.6; H, 3.0. $C_{16}H_8Cl_2$ requires C, 70.8; H, 3.0%). No isomer could be isolated from the mother liquors.

3: 3'-Dichlorodiphenyldiacetylene was prepared by a very similar method, and was crystallised six times from ethyl alcohol and finally once from methyl alcohol; feathery crystals, m. p. 87.5—88.0° (corr.) (Found: C, 71.0; H, 3.0%). No isomer could be isolated.—THE DYSON PERRINS LABORATORY, OXFORD. [Received, February 14th, 1946.]
