625. *Electric Dipole Moment Studies on the Conjugation and Stereochemistry of Some Unsaturated Ketones and Aldehydes. Parts I and II.*

By J. Breeze Bentley, K. B. Everard, Ralph J. B. Marsden, and L. E. Sutton.

The electric dipole moments of twenty-three ketones and aldehydes are reported.

Aliphatic compounds are considered in Part I, wherein it is shown that conjugation and possibly hyperconjugation lead to permanent electron drifts in directions to be expected on current theories. The magnitudes of these are roughly the same in the different molecules. A quantitative comparison of the observed moments of mesityl oxide and of phorone with those calculated from the actual moments of cyclic analogues reveals that the former compounds have *cis*-configurations about the C–C single bonds, bringing the terminal methyl groups adjacent to the oxygen atoms. Mono- and di-benzylideneacetone probably also adopt this configuration. It is shown in each case that there is less steric interference with conjugation in this configuration than in the *trans*-form. On the other hand, the moments of acraldehyde, crotonaldehyde, and cinnamaldehyde are best explained on the basis of a *trans*-configuration, *i.e.*, one with the double bonds parallel to one another.

In Part II the moments of acetophenone and six methyl derivatives thereof are discussed. With these compounds the electron drifts are less obvious, and there is no evidence for hyperconjugation between the nuclear methyl groups and the carbonyl group. The steric effect of two *ortho*-methyl groups is believed to reduce conjugation in acetomesitylene relative to those acetophenones with at least one *ortho*-position free: this contrasts with the views of J. W. Baker (*J.*, 1938, 445, etc.), which are accordingly discussed. When only one *ortho*-position is occupied, the acetyl group adopts preferentially a configuration in which its oxygen atom, rather than its methyl group, is adjacent to the *ortho*-methyl group.

It is now generally conceded that the peculiar properties of aliphatic ketones and aldehydes with conjugated systems (see, *e.g.*, Gilman, "Organic Chemistry," Vol. I, Wiley, 1943, p. 672) are due to resonance between various structures involving *p*-electrons, or, in other words, to delocalised π-bonds formed from them. This view is a re-interpretation and extension of the theories propounded by Robinson and Ingold. One consequence is that "electron drifts," which may be represented as $\mathrm{C\overset{\curvearrowright}{=}C{-}C\overset{\curvearrowright}{=}O}$, should arise in the ground state of the molecule.

The following physical methods have been employed to study the various effects of this conjugation:

(1) *Thermochemical measurements.* The heats of hydrogenation of the C=C bonds in crotonaldehyde and in but-2-ene are 25 and 28 kcals./mole respectively (Dolliver, Gresham, Kistiakowsky, Smith, and Vaughan, *J. Amer. Chem. Soc.*, 1938, **60**, 440).

(2) *Ultra-violet spectroscopy.* The ionisation potentials of the non-bonded oxygen electrons and of the carbonyl *p*-electrons are 10·18 and 11·3 e.v. respectively in acetaldehyde, and 10·06 and 11·2 e.v. in acraldehyde. The $N \longrightarrow A_1$ and $N \longrightarrow V_1$ electronic transitions occur at longer wave-lengths in acraldehyde and crotonaldehyde than in acetaldehyde, and in mesityl oxide and pulegone than in acetone (Walsh, *Trans. Faraday Soc.*, 1945, **41**, 498; 1946, **42**, 68; 1947, **43**, 158).

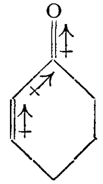
(3) *Infra-red and Raman spectroscopy.* The stretching frequency of the carbonyl bonds in mesityl oxide, phorone, and crotonaldehyde is less than in acetone and acetaldehyde (Thompson and Torkington, *J.*, 1945, 640; Hibben, "The Raman Effect and its Chemical Applications," Reinhold, 1939, p. 197).

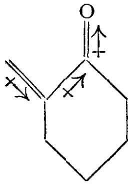
(4) *Molecular orbital* treatment of the acraldehyde molecule yields the following mobile-bond orders and π-electron distribution: $\underset{+0{\cdot}174}{\mathrm{C}}\overset{0{\cdot}920}{=\!=\!=\!=}\underset{-0{\cdot}051}{\mathrm{C}}\overset{0{\cdot}374}{-\!-\!-\!-}\underset{+0{\cdot}375}{\mathrm{C}}\overset{0{\cdot}819}{=\!=\!=\!=}\underset{-0{\cdot}495}{\mathrm{O}}$. These values should be compared with those in an unconjugated carbonyl bond: $\underset{+0{\cdot}477}{\mathrm{C}}\overset{0{\cdot}895}{=\!=\!=\!=}\underset{-0{\cdot}447}{\mathrm{O}}$ (Coulson, *Trans. Faraday Soc.*, 1946, **42**, 106; extended and checked by L. E. Orgel, unpublished calculations).

The measurement of the dipole moments of a number of such compounds was originally undertaken to provide further evidence of such resonance, which would cause the unsaturated compounds to have a moment additional to that of the saturated ones and could also cause the conjugated system to become coplanar. Both effects might be detectable.

Advantage has been taken of the fact that if the conjugated system forms part of a ring, its configuration is substantially fixed; thus the presence of a small moment in the C=C bond which is conjugated with the C=O bond would give a ketone with configuration (I) a moment larger than that of a ketone with configuration (II). These latter moments may be related by means of a set of bond moments, which may be deduced from measurements on *cyclic* ketones of known configuration, and may then be used in turn to deduce the (unknown) configurations of *open-chain* ketones and aldehydes.

(I.)





(II.)

The work on the aliphatic compounds was begun by J. B. Bentley and R. J. B. Marsden in 1931, and some of the preliminary results have been communicated by L. E. Sutton in the Faraday Society Discussion on " Dipole Moments " (*Trans. Faraday Soc.*, 1934, **30**, 789; see also *ibid.*, Appendix); these results have been revised by L. E. Sutton and K. B. Everard, and are now presented in detail, together with some recent work on *cyclo*pentanone, *cyclo*hexanone, and some nuclear-methylated acetophenones. An opportunity for studying these last compounds was provided by a gift of samples made to us by Mr. G. T. Kennedy of Trinidad Leaseholds, Ltd. The dipole moments prove to be useful in discussing steric and electronic interaction between the methyl and acetyl groups in these compounds.

EXPERIMENTAL.

(Temperatures are uncorrected unless otherwise stated.)

(Preparations by J. BREEZE BENTLEY.)

Crotonaldehyde.—A commercial specimen was thrice distilled in an atmosphere of carbon dioxide, a column being used; the fractions, b. p. 96—109°, 102—106°, and 102·4—103°, were retained. The product was dried ($MgSO_4$) between the second and the last distillation (Kekulé, *Annalen*, 1872, **162**, 97, gives b. p. 104—105°).

Mesityl Oxide (Freer and Lachman, *Amer. Chem. J.*, 1897, **19**, 887).—Acetone was saturated with gaseous hydrogen chloride and set aside overnight; the oil which separated on pouring the solution into water was washed with water (thrice), potassium hydroxide solution (thrice), and water (once), dried (Na_2SO_4), extracted with dry ether, and twice fractionated through a 5-bulb Young–Thomas column. The fraction, b. p. 127·4—128·4°, comprising nearly all the second distillate, was used {Perkin, *J.*, 1888, **53**, 587, gives b. p. 129·5—130° (corr.); Luginin, *Ann. Chim. Phys.*, 1898, [vii], **13**, 332, gives 128·39°; Mannich and Hâncu, *Ber.*, 1908, **41**, 575, give 130—131°}.

Phorone.—Claisen's method was used (*Annalen*, 1876, **180**, 4). The product was steam-distilled from calcium carbonate and then distilled. The fraction, b. p. 185—190°, was recrystallised from ligroin (b. p. 40—60°) and then had m. p. 25—27° (Baeyer, *Annalen*, 1866, **140**, 302, gives m. p. 28°).

(Preparations by RALPH J. B. MARSDEN.)

3 : 5-*Dimethyl*cyclo*hex-2-enone.*—Ethyl acetoacetate and acetaldehyde were condensed in the cold in the presence of piperidine (Knoevenagel and Klages, *Annalen*, 1894, **281**, 104; cf. Rabe and Rahm, *ibid.*, 1904, **332**, 10). The resulting diethyl 4-methylheptane-2 : 6-dione-3 : 5-dicarboxylate was boiled with an excess of 20% sulphuric acid to effect ring-closure and decarboxylation to 3 : 5-dimethyl*cyclo*hex-2-enone; this was then steam-distilled, extracted with ether, dried, and twice distilled, the fraction, b. p. 210—211°/739 mm., being used (Knoevenagel and Klages, *loc. cit.*, give b. p. 211°; Hantzsch, *Annalen*, 1882, **215**, 50, gives 208—209°; Cohnheim, *Ber.*, 1898, **31**, 1035, gives 208—210°; Wallach, *Annalen*, 1913, **397**, 199, gives 211—212°).

Pulegone.—" Pulegone Puriss." (A. Boake Roberts & Co. Ltd.) was further purified by the method of Baeyer and Henrich (*Ber.*, 1895, **28**, 652) and distilled just before use. It had b. p. 108·5°/17 mm. (Kon, *J.*, 1930, 1616, gives b. p. 109°/19 mm.).

Mesityl Oxide.—This was prepared by boiling acetone under reflux through barium hydroxide and distilling the diacetone alcohol so obtained with a trace of iodine (*Org. Synth.*, Vol. I, pp. 45, 53). The crude product was repeatedly fractionated through an efficient column, giving finally a main fraction of almost constant b. p., 128°/750 mm.

2 : 5-*Di*cyclo*pentylidene*cyclo*pentanone.*—A sample kindly provided by Dr. B. K. Blount was recrystallised several times from methanol, and then formed pale yellow needles, m. p. 81° (corr.), tending to darken on exposure to air (Wallach, *Ber.*, 1896, **29**, 2964, gives m. p. 76—77°).

Phorone.—This was made by saturating acetone with gaseous hydrogen chloride (Claisen, *loc. cit.*), distilling the crude product, recrystallising it several times from ligroin (b. p. 60—80°) with cooling, and finally centrifuging. It had m. p. 28° (corr.).

2-*Benzylidene*cyclo*hexanone.*—Wallach's results (*Ber.*, 1907, **40**, 71) could not be reproduced, owing to the 2 : 6-di- forming at the expense of the mono-benzylidene compound. The following method, in which precautions were taken to avoid evaporation of the solution, proved reasonably satisfactory. 20 G. of benzaldehyde in 50 c.c. of ethanol were added to 100 g. of *cyclo*hexanone (*ca.* 1 : 4 molar proportions) in 75 c.c. of ethanol containing 5 c.c. of 3N-sodium hydroxide. The yellow mixture was cooled in a closed flask with ice for 1½ hours, just acidified with dilute hydrochloric acid, and poured into 400 c.c. of water. The dense oil which separated was extracted with ether and distilled; the fraction,

b. p. 183—205°/26 mm., which solidified on cooling was recrystallised from ligroin and from ethanol, and then dried in a desiccator. 1·5 G. of white crystals, m. p. 54° (corr.), were obtained (Wallach, *loc. cit.*, gives m. p. 53°).

2 : 6-*Dibenzylidene*cyclo*hexanone* (Wallach, *Ber.*, 1907, **40**, 71; Vorländer and Hobohm, *ibid.*, 1896, **29**, 1837).—The results obtained by following Wallach's directions were unsatisfactory. The following method proved suitable. *cyclo*Hexanone (5 g.) and benzaldehyde (11 g.) were dissolved in ethanol (20 c.c.) and 3N-sodium hydroxide (10 c.c.) was run in; heat was evolved and the solution became brown. The solution was warmed for a few minutes on the water-bath, and on cooling almost solidified. The product, recrystallised from ethanol, formed golden-yellow crystals (6 g.), m. p. 118·5—119° (Wallach, *loc. cit.*, gives m. p. 116—118°).

2 : 5-*Dibenzylidene*cyclo*pentanone* (Vorländer and Hobohm, *loc. cit.*).—*cyclo*Pentanone (10 g.) and benzaldehyde (24 g.) were dissolved in 50% ethanol (100 c.c.), and 20% sodium hydroxide solution (25 c.c.) was added. The yellow paste which formed on stirring was washed with water and thrice recrystallised from ethanol (charcoal once), forming fluffy pale yellow crystals (10 g.), m. p. 191·3° (Vorländer and Hobohm, *loc. cit.*, give m. p. 189°).

2 : 7-*Dimethyl- and -Diphenyl-benz*cyclo*heptatrienone.*—These ketones were prepared by condensing *o*-phthalaldehyde (from *o*-xylene: Thiele and Günther, *Annalen*, 1906, **347**, 107) with distilled B.D.H. diethyl ketone and with dibenzyl ketone, respectively; the latter ketone was made by the dry distillation of calcium phenylacetate (Apitzsch, *Ber.*, 1904, **37**, 1429). The 2 : 7-dimethyl compound recrystallised from ligroin (charcoal) as white feathery plates, m. p. 85·2$_5$° (corr.) (Thiele and Weitz, *Annalen*, 1910, **377**, 7, give 85°); the diphenyl compound crystallised from ethanol as pale yellow tabular crystals, m. p. 119° (corr.) (Thiele and Weitz give m. p. 118·5°).

6-*Phenylhexa*-3 : 5-*dien*-2-*one.*—This was prepared by condensing acetone with cinnamaldehyde in presence of aqueous sodium hydroxide (Diehl and Einhorn, *Ber.*, 1885, **18**, 2320); it was twice recrystallised from ether (charcoal), forming pale yellow needles, m. p. 66·3° (corr.) (Diehl and Einhorn give m. p. 68°).

Acraldehyde.—"Acroleine Pure, stabil" (Poulenc Frères) was twice distilled in the dark at 760 mm., all corks being coated with sodium silicate (*Org. Synth.*, Vol. VI, p. 1). The fraction, b. p. 52·3—52·6°, was used (Moureu, Boutaric, and Dufraisse, *J. Chim. physique*, 1920, **18**, 333, give b. p. 52·5°/760 mm.).

Cinnamaldehyde.—A good commercial sample was fractionated from quinine under reduced pressure; it was redistilled just before use and had b. p. 121—123°/12—14 mm. (Peine, *Ber.*, 1884, **17**, 2117, gives b. p. 128—130°/20 mm.; von Reckenberg, "Einfach u. Fraktionerte Destillation," 2nd Edn., p. 300, gives b. p. 112°/8 mm.).

(Preparations by K. B. EVERARD.)

cyclo*Pentanone.*—A pure specimen kindly provided by Dr. S. G. P. Plant was fractionated; the portion used had b. p. 131°/775 mm. [Beilstein's "Handbuch" quotes b. p. 129°, 130—130·5° (corr.)].

cyclo*Hexanone.*—Water was removed from a B.D.H. specimen with potassium carbonate, and *cyclo*hexanol with calcium chloride (Walden and Birr, *Z. physikal. Chem.*, 1933, *A*, **165**, 32). The product was then fractionated twice, through a column. The portion, b. p. 156·0°/755 mm., was used (Weissberger and Proskauer, "Organic Solvents," O.U.P., 1935, give b. p. 156·1—156·8°/760 mm.). It had n_D^{25} 1·44848, whence, if d*n*/d*t* = −0·0005, $n_D^{16·8}$ is 1·4524 ("Internat. Crit. Tables," Vol. VII, p. 39, quotes $n_D^{16·8}$ 1·45242).

Methylacetophenones.—Samples supplied by Mr. Kennedy had been made by acetylating pure aromatic compounds (Noller and Adams, *J. Amer. Chem. Soc.*, 1924, **46**, 1889); they were dried ($CaCl_2$) and twice fractionated *in vacuo* just before use. Specimens used distilled over a range of <0·5°. B. p., *d*, and *n* (communicated by Mr. Kennedy) are given in Table I, with values of n_D^{20} from the literature for comparison. Since the dipole moment of 2 : 4 : 5-trimethylacetophenone appeared to be anomalous (see p. 2970), it was repurified more scrupulously by repeated fractional freezing and drying *in vacuo*. The m. p. of the pure substance was found to be 15·4$_5$° (corr.; contrast the values 10°, 11°, quoted in Beilstein's "Handbuch"), but this was depressed 0·2$_5$° after only 5 minutes' exposure in a beaker to laboratory air, showing that the compound is hygroscopic.* The m. p. in contact with water is 14·2°. The dry liquid had d_4^{25} 0·9946 and n_D^{25} 1·5375, giving $[R]_D$ 50·97 c.c. Dielectric-constant measurements on solutions of both specimens agreed.

TABLE I.

Position of Me group(s).	B. p.	Pressure, mm.	d_4^t.	*t*.	n_D^{20} (obs.).	n_D^{20} (lit.).
p-	97°	10	1·006	20	1·5335	1·5341 *
3 : 4-	105	5	—	—	1·5390	1·5388 *
2 : 5-	82	4	—	—	1·5295	1·5293 *
2 : 4-	107 †	12	0·997	22	1·5331	—
2 : 4 : 6-	110	11	0·977	17	1·5163	1·5168 ‡
2 : 4 : 5-	130	15	0·986	20	1·5396	1·5386 *

* From "Internat. Crit. Tables," Vol. VII; d*n*/d*t* assumed as −0·0005.

† Beilstein's "Handbuch" quotes 108°/12 mm. ‡ von Auwers, *Annalen*, 1919, **419**, 120.

(Preparation by P. G. EDGERLEY.)

Acetophenone.—Preliminary drying ($CaCl_2$) of a commercial specimen was followed by four fractional freezings, one-fifth being poured off each time. It was finally dried (P_2O_5) *in vacuo* overnight, and not exposed to light It had m. p. 19·2° (Livingston, Morgan, and Lammert, *J. Amer. Chem. Soc.*, 1924, **64**, 881, give m. p. 19·655°).

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* Our handling technique for liquid solutes minimises the risk of measurements being vitiated by atmospheric contamination.

PHYSICAL MEASUREMENTS, ETC.

For explanation of symbols see p. 2963.

TABLE II.

Measurements in carbon tetrachloride solution at 25°.

f_2.	*d*.	ε.	n^2.	${}_{\mathrm{T}}P_2$.	${}_{\mathrm{E}}P_2$.
		Mesityl oxide.			
		(*D*)			
0·028145	1·56017	2·5073	2·1333	187·1	30·8
0·019995	1·56703	2·4250(*I*)	2·1329	189·3	31·0
0·014133	1·57232	2·3661	2·1323	190·3	31·2
		Phorone.			
		(*D*)			
0·013363	1·56731(*I*)	2·3236(*I*)	2·1344	166·0	49·5
0·009550	1·57236	2·2956	2·1338	165·9	49·7
0·006664	1·57607	2·2748	2·1331	166·7	49·6
		Crotonaldehyde.			
0·014886	1·57525(*I*)	2·4615	2·1307	267·8	21·8
0·019231	1·57258	—	2·1306	—	21·6
0·025528	1·56831	2·6280	2·1300	257·9	21·9
0·038667	1·56008	2·8320	2·1295	246·3	20·6

TABLE III.

Measurements in benzene solution at 25°.

f_2.	*d*.	ε.	n^2.	${}_{\mathrm{T}}P_2$.	${}_{\mathrm{E}}P_2$.
		3 : 5-Dimethyl*cyclo*hexenone.			
0·036419	0·8772	3·0844	2·2539	319·0	37·6
0·035493	0·8770	3·0644	—	320·2	—
0·024645	0·8760	2·8216	2·2548	332·5	37·5
0·022833	0·8758(*I*)	2·7817	—	334·9	—
0·017329	0·8753	2·6759	2·2556	354·1	37·8
0·014902	0·8750	2·6039	2·2558	344·3	37·7
0·013565	0·8749	2·5748	2·2558	346·7	37·6
		Pulegone.			
0·020335	0·8760	2·5232	2·2588	222·6	49·8
0·018429	0·8758	2·4990	2·2588	222·7	49·9
0·011201	0·8752	2·4027	2·2582	215·7(*R*)	49·9
0·008018	0·8749	2·3714	2·2579	226·7	49·9
		Mesityl oxide.			
0·034478	0·8727$_5$	2·6452	2·2486	181·7	30·4
0·021535	0·8731	2·5051	2·2515	185·5	30·2
0·014940	0·8733	2·4338	2·2570	187·6	30·1
0·008827	0·8735	2·3680	2·2519	189·8	25·4(*R*)
		2 : 5-Di*cyclo*pentylidene*cyclo*pentanone.			
0·008131	0·8772	2·3581	2·2618	214·1	69·5
0·005462	0·8760	2·3315	2·2605	219·0	70·8
0·005060	0·8759	2·3275	2·2600	220·0	69·8
0·001427	0·8746	2·2874	2·2580	212·6(*R*)	70·1
		Phorone.			
0·025527	0·8737$_5$	2·4708	2·2567	158·1	46·4
0·018912	0·8737$_4$	2·4191	2·2568	158·5	46·4
0·013346	0·8737$_3$	2·3759	2·2570	159·0	46·5
0·007360	0·8737$_2$	2·3296	2·2570	159·7	46·4
		2-Benzylidene*cyclo*hexanone.			
0·007609	0·8769$_5$	2·3816	2·2622	257·0	60·2
0·005704	0·8761$_5$	2·3566	2·2612	263·6	60·9
0·003693	0·8754	2·3255	2·2599	258·1	60·9
0·002193	0·8747	2·3035	2·2588	253·9	60·4

TABLE III (*continued*).

f_2.	*d*.	ε.	n^2.	$_{T}P_2$.	$_{E}P_2$.
		(*D*)			
0·010086	0·8780	2·4178	—	257·4	—
0·007075	0·8765$_5$	2·3746	—	260·2	—
0·004854	0·8757	2·3422	—	260·4	—
0·003339	0·8752	2·3202	—	259·9	—
		2 : 6-Dibenzylidene*cyclo*hexanone.			
0·013618	0·8837$_5$	2·4756	2·2817	284·0	97·0
0·010666	0·8816	2·4357	2·2763	290·4	96·8
0·009975	0·8810$_5$	2·4223	2·2755	286·8	97·6
0·007775	0·8794	2·3901	2·2707	289·4	96·3
0·007637	0·8792$_5$	2·3870	2·2712	287·7	97·9
0·005697	0·8779	2·3576	2·2643	287·6	89·1
0·004599	0·8770	2·3426	2·2664	292·7	100·8
0·003330	0·8761	2·3226	2·2628	289·7	95·9
		(*D*)			
0·007850	0·8793	2·3932	2·2712	294·3	98·2
0·005601	0·8778	2·3580	2·2676	293·4	99·3
0·003771	0·8765	2·3299	2·2642	293·6	99·8
		2 : 5-Dibenzylidene*cyclo*pentanone.			
0·004506	0·8771	2·3533	2·2666	326·9	98·2
0·004286	0·8769	2·3490	2·2662	325·5	98·2
0·003156	0·8760	2·3292	2·2637	329·2	99·1
0·002633	0·8757$_5$	2·3196	2·2628	327·3	99·4
0·001873	0·8752$_5$	2·3055	2·2611	322·5	98·5
		2 : 7-Dimethylbenz*cyclo*heptatrienone.			
		(*D*)			
0·013439	0·8797	2·5351	2·2718	322·5	65·3
0·009587	0·8780$_5$	2·4594	2·2673	325·7	64·9
0·006458	0·8767	2·3979	2·2640	327·5	65·0
0·004295	0·8758	2·3559	2·2616	329·4	64·6
		(*D*)			
0·011546	0·8789	2·4983	2·2694	324·6	64·8
0·008401	0·8776	2·4368	—	327·5	—
0·005630	0·8763$_5$	2·3826	2·2630	330·3	64·6
		2 : 7-Diphenylbenz*cyclo*heptatrienone.			
		(*D*)			
0·011605	0·8846$_5$	2·5232	2·2844	382·0	110·8
0·009122	0·8823	2·4621	2·2776	373·3	109·4
0·006130	0·8795	2·3990	2·2708	374·1	109·5
0·004122	0·8776	2·3573	2·2662	375·0	109·4
		(*D*)			
0·014306	0·8872	2·5747	2·2894	373·0	109·2
0·009985	0·8831$_5$	2·4836	2·2799	377·2	109·8
0·006650	0·8800	2·4125	2·2721	379·1	109·5
0·004462	0·8779$_5$	2·3665	2·2672	381·6	110·2
		6-Phenylhexa-3 : 5-dien-2-one.			
0·007750	0·8760	2·4134	2·2654	310·3	66·0
0·005625	0·8754	2·3741	2·2632	310·3	66·2
0·003514	0·8748$_5$	2·3368	2·2609	315·4	66·2
0·003060	0·8747	2·3272	2·2603	309·6	65·8
0·001940	0·8744	2·3075	2·2592	312·3	66·1
		Acraldehyde.			
0·041118	0·8723	2·7455	2·2491	170·4	16·9
0·036156	0·8724(*I*)	2·6835	2·2506	170·8	17·0
0·020297	0·8729(*I*)	2·5005	2·2535	175·7	17·2
0·017927	0·8730(*I*)	2·4665	2·2543	171·2	17·5
0·009876	0·8732$_3$(*I*)	2·3855	—	182·96	—
		Cinnamaldehyde.			
0·022842	0·8797	2·7025	2·2681	290·3	43·9
0·012279	0·8771	2·5040	2·2631	300·2	43·5
0·007258	0·8757	2·4091	2·2606	305·0	43·8

TABLE IV.

Measurements in benzene solution at 25°.

$10^6\omega_2$.	ε_{12}.	v_{12}.	$10^6\Delta n$.
	*cyclo*Pentanone.		
8684	2·3660	1·1440	-67_3
8677	2·3657	1·1440	-67_3
3243	2·3066	1·1447	-27_2
2132	2·2951	1·1448	-18_7
	p-Methylacetophenone.		
10806	2·3643	1·1437$_6$	38_1
7839	2·3385	1·1441$_2$	27_6
5058	2·3151	1·1445$_8$	16_6
2336	2·2916	1·1448$_9$	6_6
	2 : 5-Dimethylacetophenone.		
8166	2·3220	1·1441$_9$	29_6
7002	2·3156	1·1443$_5$	26_1
5196	2·3044	1·1445$_8$	20_2
1588	2·2824	1·1451$_4$	3_9
	2 : 4-Dimethylacetophenone.		
12036	2·3500	1·1436$_8$	41_6
9890	2·3359	1·1440$_0$	34_8
7417	2·3192	1·1442$_4$	26_8
4497	2·3012	1·1446$_6$	17_1
2558	2·2885	1·1449$_1$	10_5
	2 : 4 : 5-Trimethylacetophenone.		
11643	2·3542	1·1436$_3$	45_1
8182	2·3292	1·1440$_6$	32_7
5446	2·3101	1·1443$_6$	23_0
3038	2·2938	1·1446$_9$	14_8
1185	2·2802	—	—
18265	2·4019	—	—
8739	2·3330	—	—
3312	2·2966	—	—

$10\omega^6{}_2$.	ε_{12}.	v_{12}.	$10^6\Delta n$.
	*cyclo*Hexanone.		
10751	2·3787	1·1438$_8$	-71_2
10435	2·3757	1·1439$_5$	-66_9
5394	2·3248	1·1444$_8$	-34_2
1797	2·2912	1·1448$_6$	-10_9
	Acetophenone.		
32850	—	1·1392	129_2
10115	2·3535	—	38_1
7377	2·3313	—	27_5
4678	2·3091	1·1441$_5$	15_7
2739	2·2943	1·1445	10_8
	3 : 4-Dimethylacetophenone.		
17409	2·4177	1·1429$_2$	76_6
10882	2·3640	1·1440$_0$	47_9
9322	2·3494	1·1443$_1$	41_2
5596	2·3189	1·1447$_4$	24_3
3776	2·3035	1·1450$_4$	14_9
1773	2·2866	1·1454$_4$	5_9
	2 : 4 : 6-Trimethylacetophenone.		
12917	2·3406	1·1440$_2$	16_3
10060	2·3247	1·1442$_0$	13_2
9085	2·3189	1·1443$_4$	14_0
7657	2·3123	1·1444$_8$	9_7
5174	2·2982	1·1448$_1$	7_0
4577	2·2961	—	4_7
2013	2·2827	1·1450$_6$	4_3

TABLE V.

Substance.	Formula.		${}_{\mathrm{T}}P$ old.	${}_{\mathrm{T}}P$ new.	${}_{\mathrm{E}}P$.	μ.
Crotonaldehyde (in CCl_4)	(XIV)		281·1	278·4	21·7$_5$	3·54 *
3 : 5-Dimethyl*cyclo*hex-2-enone	(III)		362·0 ± 3	365·3	37·6	4·00 †
Pulegone	(IV)		229·7 ± 0·5	236·0	49·9	3·02
Mesityl oxide	(VI)		192·6 ± 0·5	194·3	30·3	2·84
Mesityl oxide (in CCl_4)	(VI)		193·0	197·9	31·4	2·85
2 : 5-Di*cyclo*pentylidene*cyclo*pentanone	(VII)		231 ± 1	215·7	70·2	2·67
Phorone	(VIII)		160·3 ± 0·2	160·6	46·5	2·36
Phorone (in CCl_4)	(VIII)		167·0	167·8	49·7	2·40
2-Benzylidene*cyclo*hexanone	(IX)	(1 & 2)	263·5 ± 3	262·0	60·8	3·14
2 : 6-Dibenzylidene*cyclo*hexanone		(1)	297 ± 5	292·5	97·7$_5$	3·09
		(2)	293·8 ± 1		101·5	
2 : 5-Dibenzylidene*cyclo*pentanone			331 ± 5	332·2	100·0	3·36
2 : 7-Dimethyl-4 : 5-benz*cyclo*heptatrienone	(XII)	(1)	332·2$_5$ ± 0·5	337·8	64·5	3·66
		(2)	335·5 ± 0·5		64·5	
2 : 7-Diphenyl-4 : 5-benz*cyclo*heptatrienone	(XII)	(1)	376·5 ± 0·5	388·6	109·4	3·69
		(2)	384·6 ± 1		110·8	
6-Phenylhexa-3 : 5-dien-2-one			312·7$_5$ ± 3	319·6	66·0	3·52
Acraldehyde	(XIII)		186 ± 4	189·3	18·0	2·90 ‡
Cinnamaldehyde			312·4 ± 0·5	313·3	43·7	3·63 §

Previous work : * 3·67 (gas phase). † 3·79 (benzene) ; cf. *iso*phorone, which differs from (III) only by an extra 5-methyl group, 3·96 (dioxan). ‡ 2·88 (benzene), 3·04 (gas phase). § 3·71 (benzene).

These values are taken from " Tables of Electric Dipole Moments " (Technology Press, Massachusetts Institute of Technology, 1949), hereinafter referred to as M.I.T. Tables.

Table VI.

$\varepsilon_{12} = \varepsilon_1 + a\omega_2$; $v_{12} = v_1 + \beta\omega_2$; $\Delta n = \gamma\omega_2$.
(Solvent parameters are obtained by extrapolation.)

Compound.	ε_1.	a.	v_1.	$-\beta$.	$10^4\gamma$.	${}_{\mathrm{T}}P$.	${}_{\mathrm{E}}P$.	μ.
*cyclo*Pentanone	2·2718	10·836	1·14509	0·129	−740	197·0	21·6	2·93 *
*cyclo*Hexanone	2·2729	9·825	1·14505	0·108	−663	211·8	26·3	3·01 †
Acetophenone	2·2719	8·056	1·14499	0·178	+399	216·7	37·0	2·96 ‡
p-Methyl-	2·2716	8·566	1·14523	0·137	374	256·6	42·7	3·23
3 : 4-Dimethyl-	2·2718	8·392	1·14568	0·156	453	277·7	47·0	3·36
2 : 5- ,, ...	2·2729	6·052	1·14537	0·145	395	212·9	47·0	2·85
2 : 4- ,, ...	2·2719	6·473	1·14532	0·129	328	225·4	47·2	2·95
2 : 4 : 5-Trimethyl-	2·2720	7·041	1·14505	0·122	353	264·4	52·2	3·22
2 : 4 : 6- ,, ...	2·2715	5·299	1·14528	0·101	124	212·2	51·1	2·81 §

Previous work (from M.I.T. Tables, where not otherwise stated) :

* 3·00 ± 0·03 (benzene).

† (i) 2·75 (benzene), Wolf, *Z. physikal. Chem.*, 1929, *B*, **3**, 128.
(ii) 2·75 (solvent unspecified), Donle and Volkert, *ibid.*, 1930, *B*, **8**, 60.
(iii) 2·8 (benzene, 25°), Williams, *J. Amer. Chem. Soc.*, 1930, **52**, 1831.
(iv) 2·90 (dioxan), Halverstadt and Kumler, *ibid.*, 1942, **64**, 1982.
(v) 3·02 (benzene, dielectric loss method), Whiffen and Thompson, Faraday Society Discussion on " Dielectrics," 1946, p. 114.
(vi) 2·90 (benzene, dielectric loss method), Cripwell and Sutherland, *ibid.*, p. 149.

No observational data are given in papers (i) and (ii). The value 3·00 is wrongly given for (ii) in " A Table of Dipole Moments," *Trans. Faraday Soc.*, 1934, **30**, Appendix. The value 2·8 (iii) is misprinted in the original paper : the polarisations quoted therein lead to a value 2·9 [cf. paper (iv)]. In any case, in (iii) ${}_{\mathrm{T}}P_2$ was not extrapolated to infinite dilution; when this is done (by the method of Halverstadt and Kumler), the value 3·01 is obtained for μ.

‡ 2·97 (benzene) ; 2·97 (benzene) ; 2·87 (toluene) ; 2·81, 2·75 (chloroform) ; 2·85 (solvent unspecified) ; 2·90 ± 0·02 (benzene) ; 3·00 (gas phase) ; 2·77 (benzene) ; 3·67 (liquid) ; 2·96 ± 0·02 (benzene), Cherrier, *Compt. rend.*, 1947, **225**, 1306; 2·88 ± 0·03 (benzene), Kadesch and Weller, *J. Amer. Chem. Soc.*, 1941, **63**, 1310.

§ 2·71 ± 0·03 (benzene), *idem, ibid.*

Solvent purification, measurements, and computation of moments were carried out as follows : those in Table II (by J. B. B.) as described in *J.*, 1933, 652; those in Table III (by R. J. B. M.) as described in *J.*, 1936, 599; and those in Table IV (by K. B. E.) as described in this vol., p. 2312 (using a Jamin interferometer for refractive-index measurements) (see also Everard and Sutton, *Trans. Faraday Soc.*, to be published, and Hill and Sutton, this vol., p. 746, for further details). In the earlier work two dielectric-constant cells were used : a dilution cell (measurements in which are labelled *D*) and a single-solution cell. All the later work was done with the latter. As a matter of interest, total polarisations at infinite dilution have been calculated in two ways : (*a*) by the old method of extrapolating polarisation–concentration graphs, which are curved (${}_{\mathrm{T}}P$ old in Table V), and (*b*) by the more reliable method of Halverstadt and Kumler (*J. Amer. Chem. Soc.*, 1942, **64**, 2988), in which the slopes of the *rectilinear* dielectric constant– and specific volume–concentration graphs are used (${}_{\mathrm{T}}P$ new). The latter values are obtained without rejecting data, whereas in the former method some were rejected (in which case the letter *R* appears after the datum) and others either smoothed or interpolated (*I*). The difference between the two sets of polarisations, expressed as a standard deviation, is 2·2 c.c. %, the systematic error being insignificant. All dipole moments are based on the new values and are given in Debye units throughout.

Atom polarisation is ignored, and molar refractions are not extrapolated to infinite wavelength. Symbols have the usual meanings (*vide locc. cit.*). Benzene at 25° was used as solvent except in the measurements recorded in Table II, for which carbon tetrachloride at 25° was used; mesityl oxide and phorone have very nearly the same moments in both solvents. The estimated experimental uncertainties correspond to $\ngtr \pm 0{\cdot}03$ D. in the last column of Table V, and $\ngtr \pm 0{\cdot}02$ D. in Table VI.

Discussion.

Part I. Aliphatic.

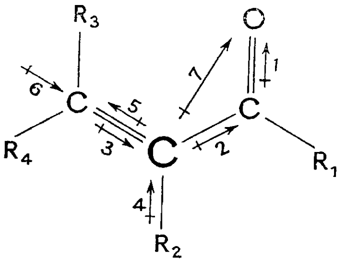
The major observations which need explaining are (*a*) that the moments of certain unsaturated ketones and aldehydes are greater than those of the corresponding saturated ones, and (*b*) that the reverse relation holds for others. It is obviously desirable that the results of our measurements should be discussed quantitatively, *i.e.*, that we should show how the observed moments can be explained as differing combinations of various component moments.

This, however, can be properly done only if the number of observations is at least equal to the number of such independent variables. In the present instance it is readily obvious that this condition is not satisfied, even if we attempt to simplify the problem by ascribing constancy to moments which are probably variable. Had simpler compounds been obtainable, some of these difficulties might have been avoided; but in actuality we have to tolerate a number of complicating side-issues.

Nevertheless, we have followed a quantitative procedure, because the complicated interrelations can thus be discussed more simply; but since there are more unknowns than observations, we can ascribe component moments only by a method of trial and error, and we cannot necessarily claim to have found the best set.

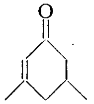
We have assumed the bond moments shown in a typical case in Fig. 1; μ_1 is the primary moment, taken as that of the saturated parent compound, *viz.*, 2·75 for acetone (M.I.T. Tables : *vide* footnote, Table II), 3·01 for *cyclo*hexanone, 2·93 for *cyclo*pentanone and 2·49 for acetaldehyde (M.I.T. Tables). μ_2 (0·1) and μ_3 (0·2) are parts of the conjugation moment; μ_4 and μ_5 (each 0·2) together correspond to the moment arising when methyl is substituted in ethylene (cf. the moments of propylene, 0·35, and of 2-methylbutadiene, 0·38; M.I.T. Tables); and μ_6 (0·6) and μ_7 (0·1) together give the moment which arises when methyl is substituted at the end of a conjugated dienoid system (cf. Hannay and Smyth, *J. Amer. Chem. Soc.*, 1943, **65**, 1931; 1946, **68**, 1357). The direction of μ_6 is as shown, save that it is taken as acting from R_4 to the middle carbon atom shown in Fig. 1 when R_3 = H instead of an alkyl group. It must be emphasised that the values of μ_2 and μ_3 have been chosen because we find them satisfactory, and that the relations between μ_4 and μ_5 and between μ_6 and μ_7 have been guessed.

FIG. 1.

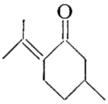


We have taken induced moments into account by the method of Hampson and Weissberger (*J.*, 1936, 393); its approximate nature needs to be stressed, especially for measurements in solution. Induction in the parent compound is already allowed for by our definition of μ_1. With the substituents, we assume that it is the groups which are polarised, and not the bonds. Refractions for the H, CH_2, Me, and Ph groups are taken as 1·1, 4·6, 5·7, and 26 c.c., respectively. The polarising dipole is assumed to be at the point of contact of the carbon and oxygen atoms (taking the covalent radii), and to be 2·4 D. in all cases. The dielectric constant of the medium is assumed to be 2·27. The geometrical details assumed for the several molecules are given in Fig. 2.

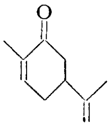
Ketones.—We will first consider cyclic compounds because they have less ambiguous configurations. The moments of *cyclo*pentanone and of *cyclo*hexanone are 2·93 and 3·01, respectively. The fact that both are larger than that of acetone (2·75) can be explained by induction, which is 0·3 in the former and 0·2 in the latter; but the reason for the observed difference between the two cyclic ketones is obscure.



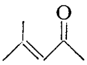
(III.)
μ = 4·00



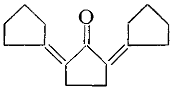
(IV.)
3·02



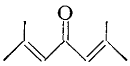
(V.)
3·17



(VI.)
2·84



(VII.)
2·67



(VIII.)
2·36

The moments of 3 : 5-dimethyl*cyclo*hex-2-enone (III) and of pulegone (IV) are 4·00 and 3·02; so, whilst the latter is nearly the same as that of *cyclo*hexanone, the former is greater by nearly 1 D. The basis already described has been chosen to give these values as the calculated moments, the difference being caused partly by the different relative orientations of the C=C and C=O bonds in the two cases, and partly by the induced moment in the methyl groups which is antiparallel to the C=O moment in pulegone ($\mu_{\text{parl.}} = -0{\cdot}14$; $\mu_{\text{perp.}} = 0{\cdot}11$) and parallel to it in the other compound ($\mu_{\text{parl.}} = +0{\cdot}06$).

The effect of moving the methyl group from position 3 (in III) to position 2 is seen in the lower moment of carvone (V) (3·17; M.I.T. Tables. Calc. : 3·44). The discrepancy may be due in part to disregard of the moment of the *iso*propenyl grouping in position 5 which should reduce the total.

In the derivatives of acetone there is no ring to prevent relative rotation of the two parts of the molecule about the single bond in the dienoid system. There is, however, likely to be restraint arising from the tendency of the system to become planar, in order that the resonance energy may be a maximum. We shall therefore compare observed moments with those calculated for the extreme configurations which this restraint could cause. These are the so-called *s-cis-* and *s-trans*-configurations (Mulliken, *Rev. Mod. Physics*, 1942, **14**, 265).

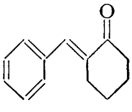
The low moment (2·84) of mesityl oxide (VI), compared with those of (III) and (IV), demonstrates that the molecule has mainly the *s-cis*-configuration shown. The calculated moments for this latter and for the *s-trans*-configuration are 2·52 and 3·88, respectively.

2 : 5-Di*cyclo*pentylidene*cyclo*pentanone (VII) has a moment of 2·67, *i.e.*, it is actually lower than that of *cyclo*pentanone, 2·93. The calculated value is, however, 3·0. Whether this discrepancy is due to the values assumed for the conjugation moments being wrong, or to inadequate allowance for induction, it is not possible to say.

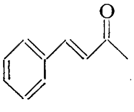
The actual moment (2·36) of phorone (VIII) is a little greater than that (2·1—2·3) predicted for the *s-cis-*, *s-cis*-configuration shown, but much less than those predicted for the *s-cis-*, *s-trans-* (3·2—3·6) and *s-trans*, *s-trans-* (4—5) configurations (the ranges of values show the uncertainty introduced by cross-conjugation : one branch may halve the conjugation moment in the other, or, at the other extreme, may leave it unaltered). Clearly, therefore, phorone has mainly the *s-cis-*, *s-cis*-configuration.

The differences between μ_{VII} and μ_{IV} or μ_{VIII} and μ_{VI} are due to neutralisation, in the former member of each pair, of moments at right-angles to the primary one.

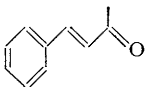
Benzylidene*cyclo*hexanone (IX) has a moment of 3·14, *i.e.*, somewhat larger than that of (IV), 3·02. The value calculated for the former is 3·19, if we assume that there is an induction moment but no conjugation moment in the benzene ring. Compared with this, benzylideneacetone (X) has a larger moment, 3·31 (M.I.T. Tables) (unlike VI compared with IV), which is greater than the values calculated for either the *s-cis-* (2·67) or the *s-trans*-configuration (XI) (3·10). The absence of alkyl groupings on carbon atom 2 in this compound allows the benzene ring to lie nearly coplanar with the rest of the conjugated system, and hence possibly to participate in the conjugation (see Fig. 2 : R_1 = Me, R_2 = R_3 = H, R_4 = Ph; cf. R_1 = R_2 = CH_2, R_3 = H, R_4 = Ph). A more quantitative discussion of this point will be deferred until other benzylidene compounds have been considered (see p. 2966). The *trans*-configurations of these compounds about the $C{=}C$ *double* bond, which are shown, are likely to be favoured for steric reasons; and the moment of (IX) confirms this.



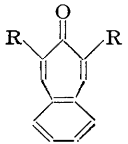
(IX.)
μ = 3·14



(X.)
3·31



(XI.)



(XII.)

The moment of 2 : 6-dibenzylidene*cyclo*hexanone (3·09) is less than the value 3·37 calculated on the assumption of induction but no conjugation in the benzene ring; the particular reason for this discrepancy, as in the case of (VII), is not obvious. The moment of 2 : 5-dibenzylidene*cyclo*pentanone (3·36) agrees well with the calculated value (3·35), again on the basis of no conjugation in the benzene ring. The moment of dibenzylideneacetone (3·28; M.I.T. Tables) is, however, larger than the value calculated on this basis for either the *s-cis-*, *s-cis-* (2·61) or the *s-cis-*, *s-trans*-configuration (2·8—3·0). It is roughly equal to that for the *s-trans-*, *s-trans*-form (3·2—3·4); but in deciding which of these configurations is adopted, we ought to consider the possible effects of conjugation involving the benzene rings, which has already been indicated in the monobenzylidene compound. This will be done when we discuss cinnamaldehyde (p. 2966).

The moments of 2 : 7-dimethyl- and 2 : 7-diphenyl-benz*cyclo*heptatrienone (XII), observed as 3·66 and 3·69, cannot usefully be calculated because of uncertainties about ring geometry and some of the component moments; but the comparison of one with the other is interesting. In both compounds there are quite large antiparallel moments arising from induction in the groups R; these are greater for R = phenyl (0·6) than for R = methyl (0·2$_4$). However, the methyl groups are likely to give rise to a further antiparallel moment because they are attached to the ends of a polyenoid system. This could account for the approximate equality of the moments of the two compounds. The moment of the unsubstituted compound (R = H) is probably about 4·3, indicating a large contribution from the conjugation of the carbonyl group with the polyenoid system.

The moment of 6-phenylhexa-3 : 5-dien-2-one (Ph·CH:CH·CH:CH·CMe:O, 3·52) compared with those of its " vinylogues " acetophenone (Ph·CMe:O, 2·96) and benzylideneacetone (Ph·CH:CH·CMe:O, 3·31) indicates that lengthening the conjugated system increases the extent of conjugation.

Aldehydes.—Hurdis and Smyth (*J. Amer. Chem. Soc.*, 1943, **65**, 89) measured the moments of several aldehydes in the gas phase; they found for acetaldehyde 2·72, for propaldehyde 2·73, and for butyraldehyde 2·72. The corresponding values in solution are 2·49, 2·54, and 2·57 (M.I.T. Tables). That of acraldehyde is 3·04 (vapour) or 2·90 (solution); and this augmentation has already been adduced as evidence of conjugation (Hurdis and Smyth, *loc. cit.*).

Although there is no possibility in aldehydes of using ring formation to fix the C=O bond in relation to the C=C bond, something can be learned about their stereochemistry by comparing the observed moments with those calculated for extreme configurations. This has already been done by Rogers (*J. Amer. Chem. Soc.*, 1947, **69**, 1243), but he has made various assumptions about the direction of his bond moments which (like ours) are not necessarily valid; and he has not actually calculated induced moments. We have included the latter, and have come to conclusions somewhat different from his.

We have taken the same basis as for the ketones (Fig. 1), and from the results in Table VII it is clear that acraldehyde † and crotonaldehyde adopt the *s-trans*-configuration,‡ but that it is impossible to say with certainty that methacraldehyde and tiglaldehyde do so.

TABLE VII.

Compound.		Formula.	$\mu_{obs.}$	$\mu_{calc.}$	
				s-cis-.	*s-trans-*.
Acraldehyde	(XIII)	CH_2:CH·CHO	2·90	2·44	2·78
Crotonaldehyde	(XIV)	Me·CH:CH·CHO	3·54	2·74	3·45
Methacraldehyde	(XV)	CH_2:CMe·CHO	2·72 *	2·85	2·38
Tiglaldehyde	(XVI)	Me·CH:CMe·CHO	3·39 *	3·10	3·09

* Rogers, *loc. cit.*

The methyl group in (XIV) is known to be *trans* to the formyl group (Blacet, Young, and Roof, *J. Amer. Chem. Soc.*, 1937, **59**, 608). The methyl groups in (XVI) are disposed *cis* about the double bond.

The moment of cinnamaldehyde is no less than 3·63. The difference between this and the moment of acraldehyde (2·90) cannot be explained by induction of a moment in the benzene ring, which is quite distant from the carbonyl dipole; the calculated values for the *s-cis-* and *s-trans*-configurations are 2·41 and 2·84, respectively. It seems essential to postulate a large contribution from conjugation of the ring with the dienoid system. The need for this has already been noted in the analogous compounds mono- and di-benzylideneacetone. It is reasonable to expect that the contribution will be the same in cinnamaldehyde and benzylideneacetone, and of a related value in dibenzylideneacetone where there is cross-conjugation. If we can show that this is in fact true, the whole picture becomes more convincing.

Assuming the magnitude of the above conjugation moment to be 0·8, and its direction to be from the centre of the benzene ring (positive pole) to the carbonyl oxygen atom (negative pole), and assuming also a *trans*-configuration about the C=C bond, we obtain the results shown in Table VIII. It is apparent that we get consistency on this basis if we assume the *s-trans*-configuration for the aldehyde, the *s-cis*-configuration for benzylideneacetone, and the *s-cis-,s-cis*-configuration for dibenzylideneacetone though the choice between this and the *s-cis-,s-trans*-configuration is not quite so clear.

On the same basis, the moments of mono- and di-benzylidene*cyclo*hexanone are calculated as 3·71 and 3·8—4·2, respectively (observed, 3·14 and 3·09). The cause of this blatant disagreement is, as we have seen on p. 2965, the steric inhibition of conjugation in these two compounds.

The Stereochemistry of the Unsaturated Ketones and Aldehydes.—From our comparisons of observed and calculated moments we have concluded definitely that in mesityl oxide the *s-cis*, and in phorone the *s-cis, s-cis*-configuration, predominate. For acraldehyde, crotonaldehyde,

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† *Added in proof.*—Dr. H. Mackle finds that a preliminary radial-distribution analysis of the electron diffraction pattern for the vapour supports the view that the *s-trans*-configuration predominates.

‡ This is equivalent to Rogers's *cis*-configuration.

and cinnamaldehyde, on the other hand, we have found *s-trans*-configurations. There is a strong indication that benzylideneacetone, like the other conjugated ketones, has an *s-cis*-,

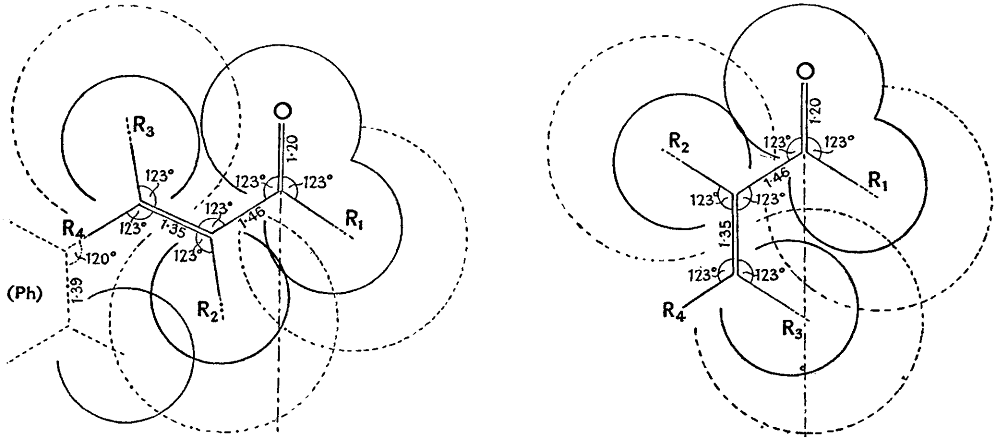
TABLE VIII.

Compound.	Formula.	$\mu_{obs.}$	$\mu_{calc.}$		
			s-cis-.	*s-trans-*.	
Cinnamaldehyde	Ph·CH:CH·CHO	3·63	3·01	3·55	
Benzylideneacetone	Ph·CH:CH·CMeO	3·31	3·25	3·80	
			s-cis-, *s-cis-*.	*s-cis-*, *s-trans-*.	*s-trans-*, *s-trans-*.
Dibenzylideneacetone	$(\mathrm{Ph{\cdot}CH{:}CH})_2\mathrm{CO}$	3·28	3·0—3·5*	3·4—4·1*	3·8—4·7*

* Range to allow for uncertainty attending cross-conjugation.

and a less strong one that the dibenzylidene compound has an *s-cis, s-cis*-configuration. It remains to consider whether these conclusions can be correlated with current theories of stereochemistry.

FIG. 2.



s-cis-. *s-trans-*.

Hydrogen atoms are shown as full lines, and methyl groups as dotted lines.

The distance C—H *is taken as* 1·09 A. *and* C—Me *as* 1·54 A. (*Pauling, " Nature of the Chemical Bond," Cornell,* 2*nd edn.,* 1945, *pp.* 161, 168); *van der Waals radii are taken as* H, 1·2; O, 1·4; Me, 2·0 A. (op. cit., *p.* 189). *The dimensions on the diagrams are based on electron-diffraction results for glyoxal and for butadiene* (*LuValle and Schomaker,* J. Amer. Chem. Soc., 1939, **61**, 3520; *Schomaker and Pauling,* ibid., p. 1769). *The same dimensions are taken for* cyclo*hexanone, but not* cyclo*pentanone, derivatives : calculations for the latter are based on the assumption of regular pentagonal rings.*

As we have previously explained (p. 2965), the driving force tending to bring the atoms of a conjugated system into a plane is the tendency of the resonance energy to become a maximum; but in such a configuration there may be steric interference energies which must be taken into account, and these may favour one or the other extreme configuration, or may in some cases prevent a coplanar configuration from being attained.

Fig. 2 shows the stereochemical relations in the *s-cis-* and *s-trans*-configurations. The full circles represent the van der Waals zones of hydrogen atoms, the dotted ones those of methyl (or methylene) groups. From this it can be seen that there is overlap of non-bonded atoms in mesityl oxide, phorone, mono- and di-benzylideneacetone, methacraldehyde, and tiglaldehyde, in either configuration. For mesityl oxide the interference is definitely less in the *s-cis-* than in the *s-trans*-form, because in the former there are two overlaps of 0·65 A., whereas in the latter there is one of 1·5 A., *i.e.*, rather more than twice as much. If the dependence of steric energy upon overlap, Δ, may be expressed as Δ^n, the ratio of the steric energies is $(2\Delta)^n/2(\Delta)^n = 2^{n-1}$, and since n is probably quite large the ratio will be at least 2.

For phorone the interference is less in the *s-cis-*, *s-cis-* than in the *s-cis-*, *s-trans*-form; the *s-trans*, *s-trans*-form is very clearly eliminated. For dibenzylideneacetone it is rather less in the *s-cis-*, *s-cis-* than in the *s-cis-*, *s-trans-*, and much less than in the *s-trans-*, *s-trans*-configuration. The *s-cis*-configuration of monobenzylideneacetone is slightly the more stable : for methacraldehyde and tiglaldehyde there is no appreciable difference. In the last four cases, where the issue is not clear-cut, the overlap in either configuration is small. For acraldehyde, crotonaldehyde and cinnamaldehyde there is no appreciable overlap at all.

Therefore, these stereochemical ideas explain convincingly the configurations found for mesityl oxide and phorone; their indications agree with those found for mono- and di-benzylideneacetone; and they are compatible with, but give no explanation of, those found for the remaining compounds.

In cases analogous to mesityl oxide it has been suggested that the carbonyl group may attract the neighbouring methyl group to give a six-membered ring, through dispersion forces and dipole attraction helped by contributions from hyperconjugated structures (see Dippy, *Chem. Reviews*, 1939, **25**, 151; Smith and McReynolds, *J. Amer. Chem. Soc.*, 1939, **61**, 1963; Baker, see p. 2969); we find no obvious need for this *ad hoc* hypothesis.

The *s-trans*-configuration, which we believe to be assumed by acraldehyde, crotonaldehyde, and cinnamaldehyde (with methacraldehyde and tiglaldehyde doubtful), has been ascribed also to butadiene, penta-1 : 3-diene, glyoxal, and diacetyl (LuValle and Schomaker, Schomaker and Pauling, Hannay and Smyth, Mulliken, *locc. cit.*; Kohlrausch and Stockmair, *Z. physikal. Chem.*, 1935, **29**, *B*, 292; Mulliken and Rieke, *Ann. Reports Prog. Phys.*, 1941, **8**, 231; Walsh, *Nature*, 1946, **157**, 768). For one of these latter (butadiene) Mulliken (*loc. cit.*), taking non-neighbour interactions into account by the molecular-orbital method, has shown that the conjugation energy is greater in the *s-trans*-configuration. Further, Aston, Szasz, Woolley, and Brickwedde (*J. Chem. Physics*, 1946, **14**, 67) have concluded from a consideration of the thermodynamic functions of butadiene that the *s-trans-* should be more stable than the *s-cis*-form, by 2·3 kcals. per mole. Doubtless also an explanation of the stability of *s-trans*-acraldehyde could be found along these lines.

Evidence for Conjugation in the Unsaturated Ketones and Aldehydes.—The variations of moment for carbonyl compounds described in the foregoing sections cannot possibly all be explained by induction. The small moments of mesityl oxide, phorone, and di*cyclo*pentylidene*cyclo*pentanone might be; but the large ones of 3 : 5-dimethyl*cyclo*hexenone, dimethyl- and diphenyl-benz*cyclo*heptatrienone, 6-phenylhexa-3 : 5-dien-2-one, acraldehyde, crotonaldehyde, and cinnamaldehyde cannot be.

The explanation we have offered, assuming conjugation moments to exist, seems much more satisfactory. This is, of course, in general agreement with the views based on either the electron-pair or the molecular-orbital treatment of such molecules. Where quantitative comparison of observed and calculated π-bond moments is possible, the agreement is poor, *e.g.*, for acetaldehyde and acraldehyde (Table IX). Such discrepancies are a common feature in comparisons of this sort (Hill and Sutton, *loc. cit.*).

TABLE IX.

Compound.	π-Bond moment. Obs.*	Calc.†
Acetaldehyde	1·5	2·6
Acraldehyde	$1{\cdot}8_4$	4·6

* Obtained by subtracting σ-bond moments of H—C (0·4) and C—O (0·8) from μ_{gas}.
† From the figures given on p. 2957.

Although we have found it essential to allow for moments when methyl groups are attached to unsaturated systems, the nature of these (*i.e.*, their direction relative to the conjugated system) is not such as to *require* that they be explained by hyperconjugation, though, on the other hand, the information that we get on this point is not sufficiently rigorous to enable us to *reject* this hypothesis, because of the complications of induction. It seems, therefore, that the possibility still remains that these moments arise from an inductive effect.

Part II. Aromatic.

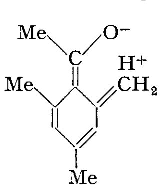
The situation is in principle somewhat simplified for aromatic compounds, because we can find the direction of the resultant moment of acetophenone by appropriate substitution in the benzene ring, provided that we can assume that the moment of neither substituent is affected by the presence of the other (Sutton and Hampson, *Trans. Faraday Soc.*, 1935, **31**, 945; Le Fèvre, " Dipole Moments," Methuen, London, 1948, p. 63). The direction of the moment of the parent compound is calculated to be within 1° of 130° to the Ph—Ac bond, from its measured moment (2·96) together with those of *p*-methylacetophenone (3·23) and toluene (0·4; this and other values are selected from M.I.T. Tables), or of *p*-chloroacetophenone (2·28; *N.B.* misprint in M.I.T. Tables: see the papers cited therein) and chlorobenzene (1·55), or of *p*-bromoacetophenone (2·29) and bromobenzene (1·55). This information may be used, together with the moment of *o*-xylene (0·54), to calculate the moment of 3 : 4-dimethylacetophenone (the method of calculation is similar to that described by Le Fèvre, *op. cit.*, p. 90; alternatively, it may be assumed that the molecule is equally probably in one of the two coplanar configurations). Since the calculated and observed moments agree within 0·06, it appears that the 3-methyl group does not much disturb the time-average of the symmetry of the acetyl group about the Ph—Ac bond.

The moment of acetone is *ca.* 2·75 along the C=O bond. The replacement of a methyl group by a phenyl thus raises the magnitude of the moment to 2·96, and alters the direction by 7° (taking the $\widehat{\text{Ph—C=O}}$ angle as 123°; Part I). The moment calculated for acetophenone on the basis described in Part I, if the moment in the benzene ring is taken as $\mu_2 + \mu_3$ (0·3), is 3·13 at 14° to the C=O direction, which is about as good agreement as can be expected from such simple calculations.

The consistency of the angle values for the acetyl group moment indicates that the several substituents Me, Cl, and Br interact very little with it. A similar negative indication is given by solution measurements of *p*-nitrotoluene and *p*-tolyl cyanide, which agree with the calculated values within less than about 0·05. This would mean that the hyperconjugation to which the moment of toluene has been attributed (Coulson, *Quart. Reviews*, 1947, **1**, 172) is not appreciably affected by the introduction of the other substituents.

There is, however, evidence that the methyl group can interact with the carbonyl group in aliphatic compounds (Part I) and in *p*-tolualdehyde (Hurdis and Smyth, *J. Amer. Chem. Soc.*, 1943, **65**, 89), though one of the measurements on which the latter case was chiefly based has been disputed (Coomber and Partington, *J.*, 1938, 1444; cf. Kadesch and Weller, *J. Amer. Chem. Soc.*, 1941, **63**, 1310). The balance of dipole-moment evidence seems to be against there being interaction between a *p*-methyl group and the other substituents, sufficient to cause a change of more than *ca.* 0·05 D.

Steric Inhibition of Resonance.—Kadesch and Weller (*loc. cit.*) find that the moment of acetomesitylene (2 : 4 : 6-trimethylacetophenone) is 0·17 lower than that of acetophenone; we confirm this, our difference being 0·15. They further find that of acetodurene to be 0·20 lower, which difference is indistinguishable from the other. They accounted for this by supposing that the *o*-methyl groups force the acetyl group out of the plane of the ring and so reduce conjugation, as Hampson and his co-workers had already suggested for other polar groups * (*J.*, 1937, 10; 1939, 981). We believe that this is the true explanation, especially in view of the striking evidence of reduced conjugation in acetomesitylene from its ultra-violet absorption spectrum (O'Shaughnessy and Rodebush, *J. Amer. Chem. Soc.*, 1940, **62**, 2906) and from its Raman spectrum (Saunders, Murray, and Cleveland, *ibid.*, 1941, **63**, 3121; 1942, **64**, 1181).



(XVII.)

On the other hand, J. W. Baker (*J.*, 1938, 445; *Trans. Faraday Soc.*, 1941, **37**, 632; Baker and Tweed, *J.*, 1941, 796), although he recognised that steric factors are certainly operative, concluded, from a survey of chemical reactivity, heats of combustion, and molecular refractions, that there is *more* conjugation in the 2 : 4 : 6- than in the 2 : 4 : 5-isomer; and he attributed this to the greater number of hyperconjugated structures (especially XVII) which can be conceived for the former. The original papers must be consulted for details, but some of the evidence put forward is as follows:

(1) 2 : 4 : 6-Trimethylacetophenone, unlike the 2 : 4 : 5-isomer, will not react with any of the usual reagents for the carbonyl group (phenylhydrazine, etc.);

(2) The (reversible) addition of a proton by sulphuric acid to the 2 : 4 : 5-isomer is complete; the addition to the 2 : 4 : 6-isomer under the same conditions is incomplete;

(3) The molecular refractions $[R]_{\alpha}$ are given as 52·7 (2 : 4 : 6-) and 50·3 c.c. (2 : 4 : 5-); and

(4) The heats of combustion of the liquid isomers are 8947 ± 6 (2 : 4 : 5-) and 8925 ± 4 (2 : 4 : 6-) cals./g., from which, with estimated values of L_v, it is concluded that the resonance energy is 0·17 e.v. (3·9 kcals./mole) greater in the latter (2 : 4 : 6-).

Observation (1) can be attributed to steric hindrance. So possibly may observation (2), but, furthermore, if the proton adds, the positive charge may be more easily delocalised in

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* The latter authors showed that the resultant of the moments induced in the methyl groups of the mesitylene and durene derivatives which they studied was either negligible or such as to augment the primary moment. We find zero resultant for the induced moment of coplanar acetomesitylene.

the 2 : 4 : 5- than in the 2 : 4 : 6-cation, because in the former the protonated acetyl group can conjugate with the ring.

Further examination of the molecular-refraction data, observation (3), shows that the value for 2 : 4 : 5- is slightly *greater* than that for 2 : 4 : 6-trimethylacetophenone (Table X), some confusion having apparently arisen previously from a mistranscription. The referees of this paper have pointed out that the value found for the latter isomer is considerably lower than the calculated one (Table X), whereas that of the former agrees.

TABLE X.

Observer(s).	2 : 4 : 5-Trimethyl-acetophenone. [R]$_{\alpha}$.	2 : 4 : 5-Trimethyl-acetophenone. [R]$_{D}$.	2 : 4 : 6-Trimethyl-acetophenone. [R]$_{\alpha}$.	2 : 4 : 6-Trimethyl-acetophenone. [R]$_{D}$.
von Auwers *	50·34	50·76	49·85	50·19
Kadesch and Weller †	—	—	—	50·25
Kennedy ‡	—	51·6	—	50·2
K. B. Everard §	—	50·97	—	—
Calculated ‖	50·35	50·75	50·45	50·85

* *Ber.*, 1912, **45**, 2764 (quoted in " International Critical Tables," Vol. VII); *Ann.*, 1919, **419**, 120 (the paper cited by Baker and Tweed, *loc. cit.*). † *Loc. cit.* ‡ Calculated from data in Table I. § P. 2959. See also Table VI. ‖ From values of n and d for acetophenone, ψ-cumene, mesitylene, and benzene quoted in " International Critical Tables," Vol. VII.

The only one of these observations which seems to us to have any weight is (4), but we think that the balance of evidence shows that conjugation of the acetyl group with the rest of the molecule is less in 2 : 4 : 6-trimethylacetophenone than in the other compounds.

The question of how far the steric effect of a single *o*-methyl group can suppress the conjugation (cf. Thomson, *J.*, 1944, 404) is, unfortunately, not answered by the dipole moment evidence, because the lowering of the moment of 2 : 5-dimethylacetophenone (2·85) relative to that of acetophenone (2·96) (which can be quantitatively explained by induction, if the conclusion at the end of the following paragraph is correct) is not accompanied by an appreciable lowering of that of 2 : 4 : 5-trimethylacetophenone (3·22) relative to that of *p*-methylacetophenone (3·23). The spectroscopic evidence on this point (O'Shaughnessy and Rodebush, *loc. cit.*) is that the relevant extinction coefficients of acetophenone and its 2 : 4-dimethyl derivative are the same (that of 2 : 4 : 6-trimethylacetophenone is one-third as much), whilst the relevant wave-length is slightly increased by the substitution (that of 2 : 4 : 6-trimethylacetophenone is decreased). Also 2 : 4 : 6-trimethylbenzaldehyde, which is sterically similar to *o*-methylacetophenones, is fully conjugated (Kadesch and Weller; Saunders, Murray, and Cleveland; *locc. cit.*). The balance of evidence therefore indicates that a single *o*-methyl group is not sufficient to prevent conjugation; and the moment of 2 : 4 : 5-trimethylacetophenone is therefore anomalous.

We should expect that the acetyl group would attempt to take up one or other of the two positions in which it is coplanar with the ring, though the *o*-methyl group prevents it from doing so completely. From the effective sizes of the acetyl oxygen and the acetyl methyl group, it appears that the group could lie more nearly coplanar if it turns the oxygen atom toward the *o*-methyl group than if it turns its methyl group thereto. When the ring portion has an unsymmetrical moment, these configurations should be distinguishable, as for instance in 2 : 4-dimethylacetophenone. In this compound, if the acetyl group could be coplanar, the moments would be 2·71 for the former configuration and 3·43 for the latter, or 3·09 for an equal mixture. The actual value is 2·95, which shows that the first configuration is the more favoured.

To sum up: the dipole-moment measurements reported herein have enabled us to make more or less definite statements about the most favoured configuration of a number of molecules, which have proved, or would prove, difficult to decide by other physico-chemical methods; and where two different methods have led to two different conclusions on stereochemical points, the dipole-moment evidence has given assistance in deciding between them.

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