# Conformations of Substituted Benzaldehydes and Acetophenones by Molecular Polarisability Measurements and Infrared Spectroscopy

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Dipole moments and molar Kerr constants at 25 °C in carbon tetrachloride solution are recorded for a series of *para*- and *meta*-substituted benzaldehydes and acetophenones. From these results, supplemented by i.r. data, information on the preferred molecular conformations of these compounds is obtained.

THIS paper reports the dipole moments and molar Kerr constants of a series of substituted benzaldehydes and acetophenones whose values are analysed to yield information concerning the preferred molecular conformations in solution. Supplementary i.r. evidence in the case of *m*-nitrobenzaldehyde, 3,4-dichloroacetophenone, and *m*-nitroacetophenone is also presented.

## EXPERIMENTAL

All the solutes were commercial. They were distilled under reduced pressure or recrystallised as appropriate, and used immediately. In the case of the benzaldehydes, all operations were conducted under nitrogen as they tend to be oxidised to benzoic acids by oxygen.

Dielectric constants, densities, and refractive indices were determined by standard procedures [1,2] and Kerr effects by the photometric method.[3] The results are in Table 1, standard notation [2] being used. The i.r. spectra were obtained with a Perkin-Elmer 337 instrument and are deposited together with detailed dielectric and electric birefringence data as Supplementary Publications No. SUP 20423 (18 pp., 1 microfiche).*

*Previous Measurements.*—The dipole moments reported agree reasonably well with literature values.[4,5] However, those of *p*-fluoroacetophenone, *m*-fluoroacetophenone, 3,4-dichloroacetophenone, *o*- and *m*-bromobenzaldehyde, and *o*- and *m*-fluorobenzaldehyde appear not to have been recorded before. The $_mK$ values of benzaldehyde and acetophenone have been reported;[6] those of *m*- and *p*-chlorobenzaldehydes and -acetophenones determined in this work may be compared with the values published [7] when our work was near completion.

## DISCUSSION

*Calculations of Molar Kerr Constants.*—Theoretical molar Kerr constants for the *para*-substituted and *meta*-substituted benzaldehydes and acetophenones were calculated for the likely structures, which are (I) for the *para*-compounds, and (II) and (III) for the *meta*-compounds. Standard procedures [2] were used in these

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are supplied as full-size copies).

[1] H. H. Huang and E. P. A. Sullivan, *Austral. J. Chem.*, 1968, **21**, 1721.

[2] R. J. W. Le Fèvre, (*a*) 'Dipole Moments,' 3rd edn., Metheun, London, 1953, ch. 2; (*b*) *Adv. Phys. Org. Chem.*, 1965, **3**, 1.

[3] H. H. Huang and S. C. Ng, *J. Chem. Soc.* (*B*), 1968, 582.

[4] A. L. McClellan, 'Tables of Experimental Dipole Moments,' W. H. Freeman and Co., San Francisco, 1963.

[5] V. Baliah and R. Aparajithan, *Tetrahedron*, 1963, **19**, 2177.

[6] P. H. Gore, P. A. Hopkins, R. J. W. Le Fèvre, L. Random, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1971, 120.

[7] C. L. Cheng, R. J. W. Le Fèvre, G. L. D. Ritchie, P. A. Goodman, and P. H. Gore, *J. Chem. Soc.* (*B*), 1971, 1198.

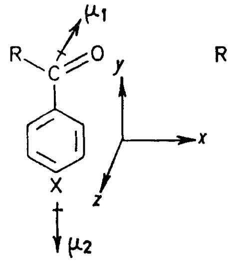
TABLE 1

Polarisations, refractions, dipole moments and molar Kerr constants at infinite dilution in carbon tetrachloride at 25 °C

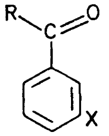
| Compound | $\alpha\varepsilon_1$ | $\beta$ | $\gamma$ | $\delta$ | ${}_2P$/c.c. | $R_D$(c.c.) | $R_D$(calc.) | $\mu$/D | $10^{12}{}_\infty(mK_2)$ |
|---|---|---|---|---|---|---|---|---|---|
| Acetophenone | 14·99 | −0·526 | 0·094 | 327 | 224·2 | 36·8 | 35·9 | 2·93 ± 0·01 | 341 ± 5 |
| *p*-Fluoroacetophenone | 8·51 | −0·392 | 0·045 | 103·1 | 159·7 | 36·0 | 35·4 | 2·44 ± 0·01 | 123 ± 2 |
| *p*-Chloroacetophenone | 8·09 | −0·227 | 0·098 | 53·5 | 168·6 | 41·2 | 40·2 | 2·48 ± 0·01 | 57 ± 3 |
| *p*-Bromoacetophenone | 6·03 | −0·029 | 0·097 | 15·4 | 164·6 | 44·7 | 43·7 | 2·40 ± 0·01 | 24 ± 0·6 |
| *p*-Nitroacetophenone | 12·95 | −0·191 | 0·108 | 329·1 | 262·4 | 42·2 | 42·5 | 3·26 ± 0·01 | 475 ± 8 |
| 4-Acetylpyridine | 10·75 | −0·472 | 0·075 | 129 | 170·4 | 34·9 | 33·9 | 2·56 ± 0·02 | 128 ± 6 |
| *m*-Fluoroacetophenone | 12·73 | −0·303 | 0·055 | 199·2 | 219·1 | 34·9 | 35·4 | 2·99 ± 0·01 | 238 ± 6 |
| *m*-Chloroacetophenone | 10·06 | −0·281 | 0·091 | 185·4 | 201·0 | 40·7 | 40·2 | 2·78 ± 0·02 | 249 ± 4 |
| *m*-Bromoacetophenone | 8·18 | −0·029 | 0·098 | 151·0 | 210·0 | 44·5 | 43·7 | 2·82 ± 0·01 | 262 ± 10 |
| *m*-Nitroacetophenone | 15·36 | −0·236 | 0·093 | 358·8 | 305·9 | 42·9 | 42·5 | 3·57 ± 0·01 | 517 ± 4 |
| 3-Acetylpyridine | 10·41 | −0·384 | 0·101 | 115 | 163·3 | 34·7 | 33·9 | 2·49 ± 0·01 | 120 ± 4 |
| *o*-Dichlorobenzene | 6·78 | −0·192 | 0·079 | 201 | 137·6 | 35·6 | 36·1 | 2·21 ± 0·01 | 259 ± 4 |
| 2,5-Dichloroacetophenone | 7·95 | −0·138 | 0·091 | 2·84 | 198·6 | 45·3 | 45·9 | 2·72 ± 0·01 | * |
| 3,4-Dichloroacetophenone | 6·97 | −0·129 | 0·097 | 79·5 | 178·7 | 45·5 | 45·9 | 2·53 ± 0·01 | 130 ± 4 |
| Benzaldehyde | 16·32 | −0·514 | 0·101 | 527 | 213·0 | 32·7 | 31·1 | 2·95 ± 0·04 | 490 ± 21 |
| *o*-Bromobenzaldehyde | 8·51 | 0·024 | | | 199·9 | 40·2 | 38·9 | 2·78 ± 0·01 | |
| *o*-Chlorobenzaldehyde | 12·15 | −0·266 | | | 213·5 | 37·5 | 36·1 | 2·92 ± 0·03 | |
| *o*-Fluorobenzaldehyde | 13·38 | −0·359 | | | 206·8 | 33·2 | 30·9 | 2·90 ± 0·05 | |
| *m*-Bromobenzaldehyde | 7·52 | 0·008 | 0·097 | 180 | 181·1 | 40·1 | 38·9 | 2·61 ± 0·06 | 291 ± 15 |
| *m*-Chlorobenzaldehyde | 10·27 | −0·251 | 0·104 | 208 | 185·1 | 37·2 | 36·1 | 2·67 ± 0·01 | 255 ± 13 |
| *m*-Fluorobenzaldehyde | 11·96 | −0·333 | 0·051 | 289 | 187·5 | 31·5 | 30·9 | 2·75 ± 0·02 | 313 ± 30 |
| *m*-Nitrobenzaldehyde | 15·88 | −0·204 | 0·125 | 342 | 278·6 | 40·3 | 37·6 | 3·46 ± 0·02 | 451 ± 8 |
| *p*-Bromobenzaldehyde | 4·64 | 0·015 | 0·121 | 133 | 124·3 | 42·0 | 38·9 | 1·98 ± 0·02 | 217 ± 26 |
| *p*-Chlorobenzaldehyde | 6·00 | −0·261 | 0·125 | 164 | 121·9 | 38·8 | 36·1 | 1·99 ± 0·01 | 202 ± 9 |
| *p*-Fluorobenzaldehyde | 6·66 | −0·372 | 0·065 | 176 | 118·7 | 33·2 | 30·9 | 2·02 ± 0·02 | 192 ± 8 |
| *p*-Nitrobenzaldehyde † | 4·38 | 0·341 | 0·049 | 2·43 | 158·5 | 39·7 | 37·6 | 2·39 ± 0·01 | 262 ± 10 |

* Indistinguishable from zero. † In $C_6H_6$.

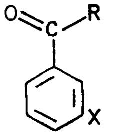
calculations by tensor addition of the bond and group polarisabilities listed in Table 2 and with reference to the arbitrary axis system shown. It was thought reasonable to assume normal valence angles of 120° around the carbonyl carbon atom. When the experimental molar refraction exceeded the value calculated from standard bond and group values[8] as in Table 3, allowance was made for exaltation of polarisability when computing the molar Kerr constants. The calculated molar Kerr constants for structures (I)—(III) are in Table 4.



(I)



(II)



(III)

TABLE 2

Anisotropic polarisabilities of bonds and groups *

| Bond or group | $b_L$ | $b_T$ | $b_V$ | Ref. |
|---|---|---|---|---|
| C–H | 0·65 | 0·65 | 0·65 | *a* |
| C–C | 0·97 | 0·26 | 0·26 | *a* |
| C=O | 2·30 | 1·40 | 0·46 | *a* |
| Ph | 10·56 | 10·56 | 6·72 | *a* |
| $C_{Ph}$–$NO_2$ | 5·04 | 2·60 | 1·31 | *b* |
| C–$C_6H_4$–F | 12·37 | 10·25 | 6·95 | *c* |
| C–$C_6H_4$–Cl | 15·50 | 11·60 | 8·30 | *c* |
| C–$C_6H_4$–Br | 17·10 | 12·40 | 9·10 | *c* |
| C–Py | 11·02 | 10·01 | 6·06 | *d* |

* Polarisabilities are quoted throughout in $10^{-24}$ cm$^3$ units (Å$^3$) and molar Kerr constants in $10^{-12}$ e.s.u.

[a] R. J. W. Le Fèvre, B. J. Orr, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1966, 273. [b] K. E. Calderbank, R. J. W. Le Fèvre, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1968, 503. [c] R. J. W. Le Fèvre and L. Radom, *J. Chem. Soc.* (*B*), 1967, 1295. [d] K. K. Chiu, Thesis, University of Singapore.

TABLE 3

Exaltations of refraction and polarisability

| | $R_D$(obs) | $R_D$(calc) | $10^{24}\Delta b$/ cm$^3$ |
|---|---|---|---|
| *p*-Fluorobenzaldehyde | 33·2 | 30·9 | 2·2 |
| *p*-Chlorobenzaldehyde | 38·8 | 36·1 | 2·8 |
| *p*-Bromobenzaldehyde | 42·0 | 38·9 | 3·1 |
| *p*-Nitrobenzaldehyde | 39·7 | 37·6 | 2·4 |
| *p*-Fluoroacetophenone | 36·0 | 35·4 | 0·7 |
| *p*-Chloroacetophenone | 41·2 | 40·2 | 1·2 |
| *p*-Bromoacetophenone | 44·7 | 43·7 | 1·2 |
| *p*-Nitroacetophenone | 42·2 | 42·5 | 0·8 |
| 4-Acetylpyridine | 34·9 | 33·9 | 1·2 |
| *m*-Fluorobenzaldehyde | 31·5 | 30·9 | 0·7 |
| *m*-Chlorobenzaldehyde | 37·2 | 36·1 | 0·9 |
| *m*-Bromobenzaldehyde | 40·1 | 38·9 | 1·0 |
| *m*-Nitrobenzaldehyde | 40·3 | 37·6 | 3·0 |
| *m*-Fluoroacetophenone | 34·9 | 35·4 | |
| *m*-Chloroacetophenone | 40·7 | 40·2 | 0·6 |
| *m*-Bromoacetophenone | 44·5 | 43·7 | 1·0 |
| *m*-Nitroacetophenone | 42·9 | 42·5 | 0·5 |
| 3-Acetylpyridine | 34·7 | 33·9 | 1·0 |
| 2,5-Dichloroacetophenone | 45·3 | 45·9 | |
| 3,4-Dichloroacetophenone | 45·5 | 45·9 | |

para-*Substituted Benzaldehydes*.—Since these benzaldehydes may reasonably be expected to exist as resonance-stabilised planar forms of (I), the dipole moments and molar Kerr constants for these planar structures were first calculated. The dipole moment of (I) is the vector resultant of components $\mu_1$ and $\mu_2$ having the same magnitudes and directions as the moments of benzaldehyde (2·95 D) and PhX respectively. Although $\mu_2$ unquestionably acts along C–X, $\mu_1$ is known to be directed

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[8] W. T. Cresswell, G. H. Jeffery, J. Leicester, and A. I. Vogel, *J. Chem. Soc.*, 1952, 514.

at an angle of *ca.* 20° to the C=O bond. The actual values of this angle for the various *para*-substituted benzaldehydes in Table 4 emerge as in Table 5, when the resultant moment of known values of $\mu_1$ and $\mu_2$, which is a function of the angle subtended by these two vectors, is equated with the observed moment.

In the case of the fluoro-, chloro-, and bromo-compounds the calculated ${}_{\mathrm{m}}K$'s ($\times 10^{12}$), exaltation not being taken into consideration, are 142, 102, and 112 respectively. When the exaltation of polarisability is assigned equally along the $X$ and $Y$ axes, the calculated ${}_{\mathrm{m}}K$'s become 206, 182, and 204 respectively, in reasonably good agreement with our experimental results (Table 1).

TABLE 4

Calculated molar Kerr constants

| Compound | Structure | Degree of non-planarity/° | $b_{xx}$ | $b_{yy}$ | $b_{zz}$ | $b_{xy}$ | $b_{yz}$ | $b_{zx}$ | $\mu_x$ | $\mu_y$ | $\mu_z$ | ${}_{\mathrm{m}}K$ * | ${}_{\mathrm{m}}K$ † |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *p*-Fluorobenzaldehyde | (I) | 0 | 12·97 | 14·64 | 8·050 | 0·390 | 0 | 0 | 1·73 | 1·04 | 0 | 142 | 206 |
| *p*-Chlorobenzaldehyde | (I) | 0 | 14·32 | 17·77 | 9·400 | 0·390 | 0 | 0 | 1·86 | 0·71 | 0 | 102 | 182 |
| *p*-Bromobenzaldehyde | (I) | 0 | 15·12 | 19·37 | 10·20 | 0·390 | 0 | 0 | 1·80 | 0·83 | 0 | 112 | 204 |
| *p*-Nitrobenzaldehyde | (I) | 0 | 15·06 | 18·41 | 8·97 | 0·390 | 0 | 0 | 1·82 | −1·55 | 0 | 214 [a] | 249 [a] |
| *p*-Fluoroacetophenone | (I) | 20 | 15·03 | 16·59 | 9·85 | 0·280 | 0·100 | 0·620 | 2·24 | 0·19 | 0·81 | 118 | 132 |
| *p*-Chloroacetophenone | (I) | 20 | 16·38 | 19·72 | 11·20 | 0·280 | 0·100 | 0·620 | 2·24 | 0·10 | 0·81 | 67 | 80 |
| *p*-Bromoacetophenone | (I) | 20 | 17·18 | 21·32 | 12·00 | 0·280 | 0·100 | 0·620 | 2·24 | 0·19 | 0·81 | 51 | 56 |
| *p*-Nitroacetophenone | (I) | 20 | 17·55 | 20·14 | 10·54 | 0·280 | 0·100 | 0·620 | 2·24 | −2·24 | 0·81 | 425 | 440 |
| 4-Acetylpyridine | (I) | 20 | 14·79 | 15·24 | 8·96 | 0·280 | 0·100 | 0·620 | 2·24 | −0·74 | 0·81 | 162 | 186 |
| *m*-Fluorobenzaldehyde | (II) | 0 | 14·02 | 13·59 | 8·05 | −0·217 | 0 | 0 | 3·07 | 1·58 | 0 | 383 | 430 |
|  | (III) | 0 | 14·02 | 13·59 | 8·05 | −0·997 | 0 | 0 | −0·73 | 1·58 | 0 | 144 | 159 |
| *m*-Chlorobenzaldehyde | (II) | 0 | 16·70 | 15·38 | 9·40 | −0·987 | 0 | 0 | 3·26 | 1·47 | 0 | 428 | 499 |
|  | (III) | 0 | 16·70 | 15·38 | 9·40 | −1·767 | 0 | 0 | −0·53 | 1·47 | 0 | 139 | 157 |
| *m*-Bromobenzaldehyde | (II) | 0 | 18·10 | 16·38 | 10·20 | −1·334 | 0 | 0 | 3·20 | 1·50 | 0 | 414 | 488 |
|  | (III) | 0 | 18·10 | 16·58 | 10·20 | −2·114 | 0 | 0 | −0·59 | 1·50 | 0 | 166 | 186 |
| *m*-Nitrobenzaldehyde | (II) | 0 | 17·34 | 16·39 | 8·76 | −0·667 | 0 | 0 | 5·30 | 0·29 | 0 | 1475 | 2012 |
|  | (III) | 0 | 17·34 | 16·39 | 8·76 | −1·447 | 0 | 0 | 1·51 | 0·29 | 0 | 134 | 183 |
| *m*-Fluoroacetophenone | (II) | 21 | 16·09 | 15·54 | 9·85 | −0·330 | −0·100 | 0·620 | 3·54 | 0·92 | 0·86 |  | 486 |
|  | (III) | 21 | 16·09 | 15·54 | 9·85 | −0·890 | 0·100 | −0·620 | −1·02 | 0·92 | 0·86 |  | 80 |
| *m*-Chloroacetophenone | (II) | 23 | 18·51 | 17·70 | 10·93 | −0·100 | −0·140 | 0·760 | 3·71 | 0·72 | 0·98 |  | 605 |
|  | (III) | 23 | 18·51 | 17·70 | 10·93 | −0·140 | 0·140 | −0·760 | −0·85 | 0·72 | 0·98 |  | 74 |
| *m*-Bromoacetophenone | (II) | 25 | 20·50 | 18·78 | 12·09 | −0·180 | −0·140 | 0·760 | 3·49 | 0·92 | 1·10 |  | 685 |
|  | (III) | 25 | 20·50 | 18·78 | 12·09 | −0·600 | 0·140 | −0·760 | −0·87 | 0·92 | 1·10 |  | 38 |
| *m*-Nitroacetophenone | (II) | 15 | 18·40 | 18·16 | 10·10 | −0·670 | −0·060 | 0·440 | 5·76 | −0·26 | 0·61 |  | 2049 |
|  | (III) | 15 | 18·40 | 18·16 | 10·10 | −0·143 | 0·060 | −0·440 | 1·10 | −0·26 | 0·61 |  | 81 |
| 3-Acetylpyridine | (II) | 29 | 15·33 | 16·60 | 8·890 | 0·040 | −0·520 | 0·060 | 4·23 | 0·44 | 1·10 |  | 459 |
|  | (III) | 29 | 15·33 | 16·60 | 8·890 | −0·220 | 0·520 | −0·060 | −0·09 | 0·44 | 1·10 |  | −52 |
| 2,5-Dichloroacetophenone | (VI) | 23 | 21·55 | 19·07 | 11·89 | 2·610 | −0·140 | 0·760 | 2·02 | 1·44 | 0·98 |  | 576 |
|  | (VII) | 23 | 21·55 | 19·07 | 11·89 | 2·190 | 0·140 | −0·760 | −2·02 | 1·44 | 0·98 |  | 125 |
| 3,4-Dichloroacetophenone | (IV) | 23 | 20·37 | 21·69 | 12·82 | 0·700 | −0·330 | 1·840 | 3·29 | −0·26 | 0·98 |  | 505 |
|  | (V) | 23 | 20·37 | 21·69 | 12·82 | −1·110 | −0·050 | 0·320 | −1·07 | −0·26 | 0·98 |  | −32 |
| *o*-Dichlorobenzene |  |  | 15·46 | 16·50 | 9·570 | 0·910 | 0·190 | −1·080 | 1·91 | 1·11 | 0 |  | 261 |

* Calculated without exaltation, from the component molecular polarisability matrix elements given in the Table. † Calculated with exaltation.

[a] Calculated from the group polarisabilities for $C_{ph}$–$NO_2$ in M. J. Aroney, H. H. Huang, R. J. W. Le Fèvre, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1966, 416.

TABLE 5

|  | $\mu_2$ | Angles between C=O and $\mu_1$ in Benzaldehydes | Angles between C=O and $\mu_1$ in Acetophenones |
|---|---|---|---|
| PhF | 1·45 | 24 | 4 |
| PhCl | 1·65 | 21 | 2 |
| PhBr | 1·52 | 22 | 5 |
| $PhNO_2$ | 3·96 | 24 | 6 |
| $C_5H_5N$ | 2·39 |  | 4 |

For *p*-nitrobenzaldehyde, it seems to be more reasonable to assign the exaltation of polarisability entirely along the C–$NO_2$ bond, in keeping with the powerful ($-I$, $-M$) effect of the $NO_2$ group. This leads to ${}_{\mathrm{m}}K = 249 \times 10^{-12}$ which compares favourably with the experimental value of $262 \times 10^{-12}$. Other approaches to the problem, such as regarding the formyl group as a freely rotating unit, or assigning the exaltation of polarisability in the direction of the formyl group, result in poorer agreement with experiment.

We therefore conclude that the results for the *para*-substituted benzaldehydes support planar structures for all these compounds.

para-*Substituted Acetophenones.*—The available evidence [9] supports a planar conformation for acetophenone which is stabilised by resonance interaction between the acetyl group and the benzene ring. Although it has been suggested that the dipole moment of acetophenone (2·93 D) itself acts at an angle of about 10° to the C=O bond,[10] for the purpose of Kerr constant calculations, the direction of the resultant vector of $\mu_1$ (2·93 D) and $\mu_2$ (I) is determined by equating it with the observed moment. Initially we calculate ${}_{\mathrm{m}}K$'s for coplanar structures for the *para*-substituted acetophenones. With the exaltation of polarisability assigned along the $X$-axis, the ${}_{\mathrm{m}}K$'s ($\times 10^{12}$) are: X = F, 183; Cl, 146; Br, 131; $NO_2$, 566; and 4-acetylpyridine, 288. Comparison with Table 1

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[9] P. H. Gore, P. A. Hopkins, R. J. W. Le Fèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1971, 120.

[10] J. B. Bentley, K. B. Everard, R. J. B. Marsden, and L. E. Sutton, *J. Chem. Soc.*, 1949, 2957.

shows that the calculated values are all substantially higher than the observed values. However, agreement between calculated and observed values can be achieved by rotating the C–CO–C plane away from the aromatic plane. The angles of rotation necessary for this purpose are summarised in Table 6. Thus it is seen that the *para*-substituted acetophenones are all effectively non-planar, in agreement with an earlier report for *p*-chloroacetophenone.[7] The explanation offered for *p*-chloroacetophenone, that an electron-withdrawing group causes a lowering of the barrier to internal rotation by reducing the mesomeric interaction of the acetyl group with the aromatic ring, seems to be applicable for all the compounds considered here.

TABLE 6

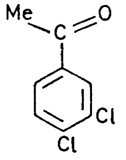
*cis–trans*-Population distribution

| | | *meta*-X-acetophenones | | | | | *meta*-X-benzaldehydes | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| X | | F | Cl | Br | $NO_2$ | (3-Acetylpyridine) | F | Cl | Br | $NO_2$ |
| Dihedral angle (between C–CO–C plane and aromatic plane) | | 21° | 23° | 25° | 15° | 29° | 0 | 0 | 0 | 0 |
| Dipole moments | % *cis*(II) | 55 | 42 | 45 | 35 | 27 | 54 | 45 | 42 | 37 |
| | % *trans*(III) | 45 | 58 | 55 | 65 | 73 | 46 | 55 | 58 | 63 |
| Kerr constant | % *cis*(II) | 39 | 33 | 35 | 22 | 34 | 57 | 28 | 35 | 15 |
| | % *trans*(III) | 61 | 67 | 65 | 78 | 66 | 43 | 72 | 65 | 85 |

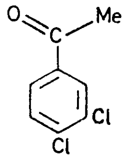
meta-*Substituted Benzaldehydes*.—Several workers [11,12] have concluded from i.r. spectral studies of rotational isomerism in *m*-halogenobenzaldehydes that in both the liquid and vapour state two conformers are present and that the *cis*-forms (II) of *m*-chloro- and *m*-bromobenzaldehyde are more stable than the *trans*-forms (III). This contrasts with the earlier deduction of Karabatsos and Vane [13] from $^1H$ n.m.r. coupling constants that the *trans*-form (III) is the more stable species. More recently, however, polarisability measurements on *m*-chlorobenzaldehyde [7] have supported the n.m.r. work. We now analyse our results for the *meta*-substituted benzaldehydes using the same dipole-moment components, polarisabilities, and assignment of exaltation of polarisability as in the case of the *para*-substituted benzaldehydes, with the conclusions shown in Table 6. They confirm that in $CCl_4$ solution, the *trans*-form is energetically the more favoured structure for the *meta*-substituted benzaldehydes except *m*-fluorobenzaldehyde, where the distribution is approximately equimolecular.

meta-*Substituted Acetophenones*.—Since our results for the *para*-substituted acetophenones have indicated that these molecules are probably non-planar, we have carried out an analysis for the *meta*-substituted acetophenones assuming appropriate non-planar forms of *cis*-(II) and *trans*-(III) with dihedral angles as given in Table 4. Again, although the results based on dipole moments alone generally differ somewhat from those based on Kerr constants, the general conclusion can be drawn that the *trans*-(III) form predominates in solution, except in the case of *m*-fluoroacetophenone where the dipole-moment data suggest a distribution somewhat in favour of the *cis*-(II) form.

In order to interpret the results for 3,4-dichloroacetophenone, we consider first the data for *o*-dichlorobenzene. Bastiansen and Hassel [14] concluded from their electron-diffraction measurements that the two chlorine atoms are bent out of the plane of the ring by 18° with the two chlorine atoms on opposite sides of the ring plane. If we adopt this model, the $_mK$ of *o*-dichlorobenzene calculated on this basis turns out to be 261 which is in satisfactory agreement with the observed value of 259. We accordingly assume that the *ortho*-chlorines are similarly disposed in 3,4-dichloroacetophenone. For a dihedral angle of 23° the *cis* : *trans* ratio derived from the experimental data emerges as 44 : 56 (dipole moment) and 30 : 70 (Kerr constant), *i.e.*, with the *trans*-isomer as the more stable species. These results are in close agreement with those for *m*-chloroacetophenone (Table 6).

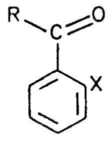


(IV)

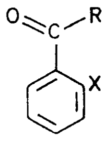


(V)

ortho-*Substituted Benzaldehydes and* 2,5-*Dichloroacetophenone*.—The *o*-halogenobenzaldehydes can exist in two rotational isomeric forms (VI) and (VII). The possibility of intramolecular hydrogen bonding aided by resonance stabilisation, and consideration of steric



(VI)



(VII)

X = F, Cl, Br

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effects based on scale models, suggests that the *trans*-isomer (VI) should be favoured over the *cis*-isomer (VI). The calculated dipole moments for structure (VII) are: X = F, 3·02 D; Cl, 3·10 D; and Br, 3·07 D; for structure (VI) they are: X = F, 4·24 D; Cl, 4·47 D; and Br, 4·39 D. Since the observed dipole moments are only slightly smaller than the values calculated for the *trans*-structures, our experimental results suggest that the *o*-halogenobenzaldehydes exist entirely in the *trans*-conformation.

The observed moment of 2,5-dichloroacetophenone (2·72 D) is somewhat smaller than that of acetophenone (2·93 D). Although we cannot distinguish between *cis*- and *trans*-conformations for this molecule on the basis of dipole moments alone, its smaller dipole moment suggests a smaller degree of mesomeric interaction between the acetyl group and the benzene ring and therefore favours a non-planar structure. By analogy with *o*-chloroacetophenone[7] a dihedral angle of about 45° may be assumed. Using this angle and from the observed ${}_{\mathrm{m}}K$ value of *ca.* 0 and the calculated ${}_{\mathrm{m}}K$'s for the *cis*- and *trans*-conformations (Table 4) we obtain a *cis* : *trans*-ratio of *ca.* 14 : 86. This is however not a unique solution as several undetermined variables are involved.

*Spectroscopic Discussion.*—Previous i.r. spectroscopic work[11,12,15,16] supports the view that rotational isomerism occurs in the *m*-halogeno-benzaldehydes and -acetophenones. The i.r. spectra of *m*-nitrobenzaldehyde, *m*-nitroacetophenone, and 3,4-dichloroacetophenone obtained in this work for the solids and solutions seem best interpreted in terms of the existence of these compounds in two rotational isomeric forms in solution. Further, by analogy with the *m*-halogenobenzaldehydes, the presence of extra bands in solution suggest the existence of only one form in the solid state.

In the case of *m*-nitrobenzaldehyde, comparison of the solid and solution spectra shows that the solution-state bands at 708, 900, 1158, 1285, 1730, 2800, and 2825 cm$^{-1}$ are missing from the solid-state spectrum. The presence of two carbonyl stretching vibrations at 1710 and 1730 cm$^{-1}$ is a good indication of the presence of two isomers, the *cis*-(II) and *trans*-(III) forms. In the solid-state spectrum however, we note besides the presence of a carbonyl band at 1709 another band at 1690 cm$^{-1}$. It seems unlikely that the latter band is due to a carbonyl stretching vibration because the solid-state spectrum of *p*-nitrobenzaldehyde (in which *cis–trans*-isomerism does not arise) also shows two bands in this region, at 1710 cm$^{-1}$ and at 1680 cm$^{-1}$, and only the former has been recognised[17] as corresponding to a carbonyl stretching vibration.

In order to determine which set of bands is due to the *trans*- or *cis*-forms, i.r. spectra were obtained for solutions of *m*-nitrobenzaldehyde in solvents of different dielectric constants. It was observed that the intensity of the 1710 cm$^{-1}$ band increased with respect to that of the 1730 cm$^{-1}$ band as the dielectric constant of the solvent increased. This could mean that the lower-frequency band at 1710 cm$^{-1}$ is due to the more polar rotamer, namely the *cis*-form. In the solid state, only the 1710 cm$^{-1}$ carbonyl band is evident, suggesting the presence of only the *cis*-form in that state.

There are two lone-hydrogen out-of-plane wag bands at 900 and 904 cm$^{-1}$ in the solution spectrum and only one band at 918 cm$^{-1}$ in the solid-state spectrum. The absence of the low-frequency band from the solid-state spectrum is another good indication of the presence of only one isomer in the solid state.

In the case of *m*-nitroacetophenone and 3,4-dichloroacetophenone the extra bands in solution are 903, 935, 1290, and 3000 cm$^{-1}$ and 530, 905, 968, and 2560 cm$^{-1}$ respectively. In contrast to *m*-nitrobenzaldehyde, the single-band character of the carbonyl stretching frequency is apparently preserved in solution as well as in the solid state. It appears that the vibrational frequencies of this particular band for the two species in solution are not sufficiently well-separated for them to be resolved effectively. The band at *ca.* 900 cm$^{-1}$ missing from the solid-state spectrum is present in solution for all three compounds. The i.r. evidence in this section therefore is consistent with the occurrence of the compounds in the two specified conformations in solution but in only one in the solid state.

[2/282 *Received, 7th February,* 1972]

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