# ZWITTERION-STRUCTURES IN UNSATURATED CARBONYL COMPOUNDS.

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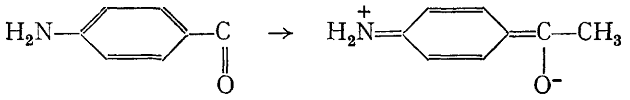
In a previous paper,[1] attention has been drawn to the fact that the unexpectedly high dipole-moment (4·29D) of *p*-amino-acetophenone may be accounted for by the assumption that an electron shift has taken place towards a Zwitterion-structure (I → II) :



I. II.

which naturally would exhibit an unusually high electric moment. It is to be expected that analogous, perhaps even more pronounced effects would appear in α, β-unsaturated aldehydes and ketones in which the conjugated system is terminated by an amino group.[2] This expectation has been verified by the investigation of the following compounds :—

| | | |
|---|---|---|
| *p*-dimethylamido-benzaldehyde | $Me_2N . C_6H_4 . CHO$ | 5·6D |
| *p*-dimethylamido-cinnamic aldehyde | $Me_2N . C_6H_4 . CH{=}CH . CHO$ | 5·4D |
| *p*-dimethylamido-benzylidene-acetone | $Me_2N . C_6H_4 . CH{=}CH . CO . CH_3$ | 5·3D |
| *p*-dimethylamido-cinnamylidene-acetone m.p. 120° | $Me_2N . C_6H_4 . CH{=}CH . CH{=}CH . CO . CH_3$ | 6·7D |
| *p*-dimethylamido-benzal-acetophenone | $Me_2N . C_6H_4 . CH{=}CH . CO . C_6H_5$ | 4·3D |
| *p*-dimethylamido-cinnamylidene-acetophenone | $Me_2N . C_6H_4 . CH{=}CH . CH{=}CH . CO . C_6H_5$ | 5·4D |

The effect appears to be more marked with increasing number of double bonds in the conjugated system of the ketones. The same seems to be true for the pair

| | | |
|---|---|---|
| ethyl *p*-amino-benzoate | $H_2N . C_6H_4 . COOC_2H_5$ | 4·0 [3] |
| ethyl *p*-dimethylamino-cinnamate | $Me_2N . C_6H_4 . CH{=}CH . COOC_2H_5$ | 4·6 ; |

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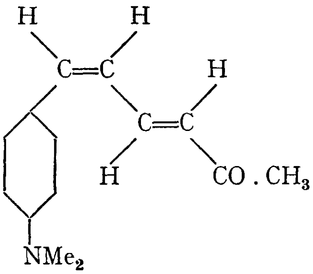
[1] Bergmann and Weizmann, *Trans. Faraday Soc.*, 1936, **32,** 1318.

[2] Compare Burawoy, *Ber.*, 1932, **65,** 941, 947.

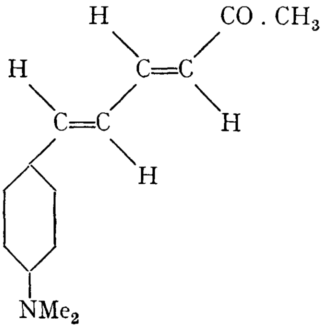
[3] Estermann (*Z. physik. Chem. B.*, 1938, **1,** 134) reported the dipole moment 3·3D for methyl *p*-amino-benzoate.

in this case, too, the figures are higher than simple addition of the moments of the amino and the carbethoxy groups would let us expect. In this respect, the C=O group of the carboxyl behaves like an aldehydic or ketonic carbonyl.

Of *p*-dimethylamido-cinnamylidene-acetone, we have been able to isolate besides the substance listed in the above table a second of the four possible geometric isomers; m.p. 215°. Its dipole moment is distinctly lower (2·4D). This is understood if the polar groups occupy a *cis*-position with regard to each other, *e.g.* III instead of IV.



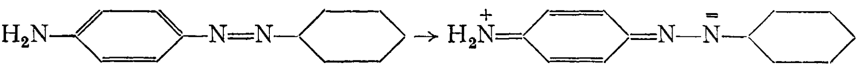
III.



IV.

In connection with these experiments, we have determined the electric moment of *m*-amino-acetophenone; its magnitude (5·4D) seems to indicate that a similar effect occurs as with the isomeric *para*-compound, although no *meta*-quinoidic formulation of this substance is possible.

The intense colour developed by the nitrogen-terminated conjugated systems in, *e.g.*, sulphuric acid, may well be ascribed to a stabilisation of the quinoidic arrangement by addition of the elements of the acid to the charged system.[4] In this connection attention may be drawn to the salt-formation of amino-azo-dyes; for these substances, we have advanced previously the suggestion that they, too, undergo an electron shift in accordance with the scheme V → VI.



V. VI.

On addition of HX, V would give the yellow salt, whereas VI, by reaction on the terminal atoms of the charged system, gives the violet isomer, discovered by Hantzsch.[5]

## Experimental.

The figures in the tables have the following significance: *c* molar fraction, $\rho$ density, $\epsilon$ dielectric constant, *n* refractive index, $P_{\frac{1}{2}}$ total polarisation ($P_{E\frac{1}{2}}$ electronic polarisation) for the solution, $P(P_E)$ the same for the solute, $P_{A+O}$ atomic and orientation polarisation, which is either graphically extrapolated to infinite dilution or of which the average is taken.

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[4] Compare, for a similar case, Wizinger, *Z. angew. Chem.*, 1927, **40**, 939.

[5] Hantzsch, *Ber.*, 1909, **42**, 2129. It may, however, be noted that according to Kehrmann (*Ber.*, 1915, **48**, 1933; *Ber.*, 1917, **50**, 856) the violet salts need not necessarily be formulated as quinoidic substances.

| $c$. | $\rho$. | $\epsilon$. | $n^2$. | $P_{\frac{1}{2}}$. | $P_{E\frac{1}{2}}$. | $P$. | $P_E$. | $P_{A+O}$. |
|---|---|---|---|---|---|---|---|---|
| ***p*-Dimethylamido-benzaldehyde**[6] ($t$ = 17·5° *Benzene*). | | | | | | | | |
| 0 | 0·8816 | 2·2830 | 2·2251 | 26·589 | — | — | — | — |
| 0·00345 | 0·8831 | 2·4815 | 2·2255 | 29·291 | — | 809 | calcd. | 763 |
| 0·00679 | 0·8846 | 2·5813 | 2·2258 | 30·624 | — | 621 | 46 | 575 |
| 0·00878 | 0·8855 | 2.7300 | 2·2261 | 32·479 | — | 698 | — | 652 |
| $P_{A+O}$ (average) = 664. $\mu$ = 5·6D. | | | | | | | | |
| ***p*-Dimethylamido-cinnamic aldehyde**[7] ($t$ = 21·3° *Benzene*). | | | | | | | | |
| 0 | 0·8771 | 2·2813 | 2·2457 | 26·611 | 26·092 | — | — | — |
| 0·00178 | 0·8788 | 2·3447 | 2·2494 | 27·530 | 26·153 | 543 | 60 | 483 |
| 0·00279 | 0·8798 | 2·3990 | 2·2503 | 28·295 | 26·172 | 630 | 55 | 575 |
| ($t$ = 27·4°). | | | | | | | | |
| 0 | 0·8699 | 2·2691 | 2·2323 | 26·656 | 26·108 | — | — | — |
| 0·00316 | 0·8713 | 2·4123 | 2·2380 | 28·767 | 26·254 | 694 | 72 | 622 |
| $P_{A+O}$ (average) = 598. $\mu$ = 5·4D. | | | | | | | | |
| ***p*-Dimethylamido-benzylidene-acetone**[8] ($t$ = 24·2° *Benzene*). | | | | | | | | |
| 0 | 0·8737 | 2·2754 | 2·2380 | 26·632 | 26·079 | — | — | — |
| 0·00280 | 0·8741 | 2·3861 | — | 28·313 | — | 627 | (86) | 541 |
| 0·00503 | 0·8744 | 2·5197 | 2·2471 | 30·210 | 26·382 | 738 | 87 | 651 |
| 0·00706 | 0·8747 | 2·5878 | 2·2500 | 31·169 | 26·492 | 669 | 85 | 584 |
| $P_{A+O}$ (average) = 592. $\mu$ = 5·3D. | | | | | | | | |
| ***p*-Dimethylamido-cinnamylidene-acetone**[9]**; m.p. 120/2°** ($t$ = 25·4° *Benzene*). | | | | | | | | |
| 0 | 1·0273 | 2·2385 | 2·0116 | 25·031 | 21·601 | — | — | — |
| 0·00136 | 1·0269 | 2·3294 | 2·0140 | 26·365 | 21·692 | 1006 | 89 | 917 |
| 0·00196 | 1·0268 | 2·3767 | 2·0150 | 27·034 | 21·727 | 1045 | 85 | 960 |
| $P_{A+O}$ (average) = 939. $\mu$ = 6·7D. | | | | | | | | |

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[6] Commercial sample; recrystallised from light-petroleum (b.p. 80-100°); m.p. 63°.

[7] Koenig and Schramek, *Ber.*, 1928, **61**, 2078. From alcohol, leaflets, m.p. 141°.

[8] In order to obtain *p*-dimethylamido-benzal-acetone, it is necessary to change the conditions stated by Sachs and Lewin (*Ber.*, 1902, **35**, 3576): 3 g. dimethylamido-benzaldehyde and 10 c.c. acetone were condensed in 6 c.c. alcohol in presence of some drops of sodium hydroxide solution. From alcohol, m.p. 135-136°. If the aldehyde is condensed with 1·5 g. acetone only, the condensation product, recrystallised from benzene-light petroleum, melts at 191-192° and is bis-(*p*-dimethylamido-benzal)-acetone (Sachs and Lewin, *l.c.*).

[9] When to a mixture of dimethylamido-cinnamic aldehyde (1·3 g.), acetone (0·3 g.) and alcohol (12 c.c.), a few drops of NaOH solution were added, crystals separated on standing which after treatment with butyl alcohol and recrystallisation from acetone, melted at 215°. The analytical figures concord with the formula of dimethylamido-cinnamylidene-acetone (Found: C, 78·1; H, 6·5. $C_{14}H_{17}ON$ requires: C, 78·1; H, 7·9 %).

In an experiment, in which 2·5 g. of the aldehyde and 10 c.c. of acetone in 12 c.c. of alcohol were condensed, the reaction product, after recrystallisation from benzene, had m.p. 120-122° and gave the same analytical figures (Found: C, 77·4; H, 7·6. $C_{14}H_{17}ON$ requires: C, 78·1; H, 7·9 %).

| $c$. | $\rho$. | $\epsilon$. | $n^2$. | $P_{\frac{1}{2}}$. | $P_{E_{\frac{1}{2}}}$. | $P$. | $P_E$. | $P_{A+O}$. |
|---|---|---|---|---|---|---|---|---|
| ***p*-Dimethylamido-benzal-acetophenone**[10] ($t$ = 20·3° *Benzene*). | | | | | | | | |
| 0 | 0·8783 | 2·2834 | 2·2440 | 26·609 | 26·061 | — | — | — |
| 0·00276 | 0·8791 | 2·3536 | 2·2515 | 27·799 | 26·279 | 457 | 105 | 352 |
| 0·00316 | 0·8794 | 2·3927 | 2·2533 | 28·358 | 26·355 | 491 | 104 | 387 |
| 0·00642 | 0·8801 | 2·5056 | 2·2596 | 30·034 | 26·578 | 560 | 106 | 454 |
| $P_{A+O}$ (average) = 398. $\mu$ = 4·4D. | | | | | | | | |
| ***p*-Dimethylamido-cinnamylidene-acetophenone**[11] ($t$ = 26·0° *Dioxan*). | | | | | | | | |
| 0 | 1·0272 | 2·2301 | 2·0135 | 24·911 | 21·634 | — | — | — |
| 0·00147 | 1·0279 | 2·2917 | 2·0203 | 25·848 | 21·796 | 660 | 132 | 528 |
| 0·00216 | 1·0282 | 2·3431 | 2·0224 | 26·590 | 21·855 | 803 | 124 | 679 |
| 0·00324 | 1·0286 | 2·3806 | 2·0278 | 27·151 | 21·983 | 716 | 129 | 587 |
| $P_{A+O}$ (average) = 598. $\mu$ = 5·4D, | | | | | | | | |
| **Ethyl *p*-amino-benzoate**[12] ($t$ = 19·4° *Benzene*). | | | | | | | | |
| 0 | 0·8794 | 2·2852 | 2·2500 | 26·603 | 26·088 | — | — | — |
| 0·00386 | 0·8813 | 2·3962 | 2·2524 | 28·229 | 26·174 | 447 | 48 | 399 |
| 0·00620 | 0·8825 | 2·4311 | 2·2512 | 28·743 | 26·193 | 372 | 49 | 323 |
| 0·00848 | 0·8837 | 2·4659 | 2·2536 | 29·247 | 26·260 | 339 | 46 | 293 |
| $P_{A+O}$ (average) = 340. $\mu$ = 4·0D. | | | | | | | | |
| **Ethyl *p*-dimethylamino-cinnamate**[13] ($t$ = 18·8° *Benzene*). | | | | | | | | |
| 0 | 0·8801 | 2·2964 | 2·2407 | 26·599 | 25·929 | — | — | — |
| 0·00480 | 0·8828 | 2·4541 | 2·2545 | 29·097 | 26·280 | 547 | 99 | 448 |
| 0·00676 | 0·8838 | 2·5312 | 2·2563 | 30·188 | 26·368 | 556 | 91 | 465 |
| $P_{A+O}$ (average) = 457. $\mu$ = 4·6D. | | | | | | | | |
| ***p*-Dimethylamido-cinnamylidene-acetone** (m.p. 215°)[9] ($t$ = 20·0° *Dioxan*). | | | | | | | | |
| 0 | 1·0284 | 2·3141 | 2·0170 | 26·065 | 21·664 | — | — | — |
| 0·00040 | 1·0314 | 2·3239 | 2·0218 | 26·138 | 21·690 | 210 | 87 | 123 |
| $\mu$ = 2·4D | | | | | | | | |
| ***m*-Amino-acetophenone**[14] ($t$ = 18·2° *Benzene*). | | | | | | | | |
| 0 | 0·8808 | 2·2876 | 2·2515 | 26·995 | 26·069 | — | — | — |
| 0·00457 | 0·8827 | 2·4541 | 2·2530 | 28·945 | 26·122 | 541 | 38 | 503 |
| 0·00747 | 0·8839 | 2·4999 | 2·2536 | 29·574 | 26·151 | 426 | 37 | 389 |
| 0·01078 | 0·8852 | 2·5435 | 2·2560 | 30·165 | 26·208 | 363 | 39 | 324 |
| $P_{A+O}$ (average) = 635. $\mu$ = 5·4D. | | | | | | | | |

[10] Sachs and Lewin, *l.c.*[8] From alcohol, m.p. 114°.

[11] Dimethylamido-cinnamic aldehyde (1 g.) and acetophenone (1·5 g.) were gently heated in alcohol (10 c.c.) in presence of a few drops of NaOH solution for 5 minutes. On cooling, brown, shiny needles separated, which after recrystallisation from methyl alcohol, had m.p. 155-157° ; yield 0·6 g. (Found : C, 83·0 ; H, 6·3. $C_{19}H_{19}ON$ requires : C, 82·3 ; H, 7·0 %).

[12] Commercial sample ; from alcohol, m.p. 91-92°.

[13] Sodium wire (2·3 g.) is suspended in ethyl acetate (20 g.) and a solution of *p*-dimethylamido-benzaldehyde (14·9 g.) in ethyl acetate (30 g.) is added. The reaction is slow, but goes to complete solution of the sodium. Glacial acetic acid (6 g.) is added, the product washed with water, dried with sodium sulphate and evaporated. The residue is recrystallised from light-petroleum (b.p. 80-100°) ; m.p. 70°. Weil, *Monatshefte*, 1908, **29**, 900.

[14] Acetophenone was nitrated according to Elson, Gibson and Johnson (*J. Chem. Soc.*, 1930, 1130) and the *m*-nitro-compound reduced in the following way : 10·5 g. were mixed with 24 g. granulated tin and gently heated. Then concentrated hydrochloric acid was added in small quantities, until all the metal had dissolved. Alkali was added and the amino-compound isolated by extraction with ether (yield, 5 g.). Recrystallisation from benzene gave slightly yellowish plates, m.p. 99°.

## Summary.

The occurrence of Zwitterion-structure is detected in compounds of the *p*-dimethyl-amido-benzaldehyde, *p*-dimethylamido-benzal-acetophenone and ethyl *p*-amino-benzoate type by means of dipole-moment measurements. The difference in electric moment of two isomeric dimethyl-amido-cinnamylidene-acetones obtained is discussed.

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