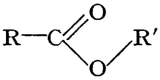
41. *The Use of Monolayer Measurements for determining Structures in Aqueous Media. The Ester and the Triazo-group.*

By A. E. Alexander.

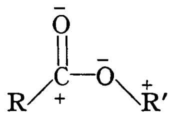
The study of monolayers of long-chain esters and of α-triazopalmitic acid has shown that both the ester and the triazo-group, which normally exist in a resonating state, lose this resonance on immersion in water and revert to one definite form. With the former it is to the classical structure  $R{-}C({=}O){-}O{-}R'$ with practically free rotation about the C—O bond, and with the latter, to the co-ordinated form $^{-}\mathrm{N}\leftarrow\mathrm{N}\equiv\mathrm{N}$.

The usual methods of determining the structure of an organic compound, *e.g.*, by *X*-ray or electron diffraction, spectra, dipole moments, etc., are carried out in the solid or the gaseous state, on in non-polar solvents, but it would appear from the examples given below that the structure thus deduced may be very different from that in an aqueous medium. From a study of monolayers, particularly of the change in phase-boundary potential brought about by spreading a monolayer upon a clean water surface, it is possible to obtain some insight into the orientation and structure of the polar head-group as it actually exists when immersed in water. This would be difficult, if not impossible, by most other methods, and is obviously of importance for understanding the reactions of organic compounds in aqueous solution, since the reactivity may be profoundly affected by any changes in the electronic structure.

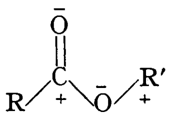
The methods used for the simultaneous force–area and potential–area measurements were those usually employed in this laboratory (see, *e.g.*, Gee and Rideal, *Proc. Roy. Soc.*, 1935, *A*, **153**, 116), and need no further elaboration.

The Ester Group.—From the comparison of the experimental dipole moments with those calculated for the *cis*- (I) and the *trans*- (II) positions, it was shown originally by Eucken and Meyer (*Physikal. Z.*, 1929, **30**, 397), and recently confirmed by Sutton and Marsden

(J., 1936, 1383), that in non-polar solvents the ester group exists solely in the *trans*-position, the locking in this position being practically complete as shown by the temperature independence of the moment. Sturtevant (*J. Amer. Chem. Soc.*, 1935, **55**, 4478) showed that the electrostatic forces between the polar groups were insufficient to account for this



(I.)



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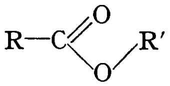

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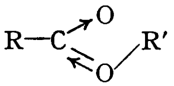
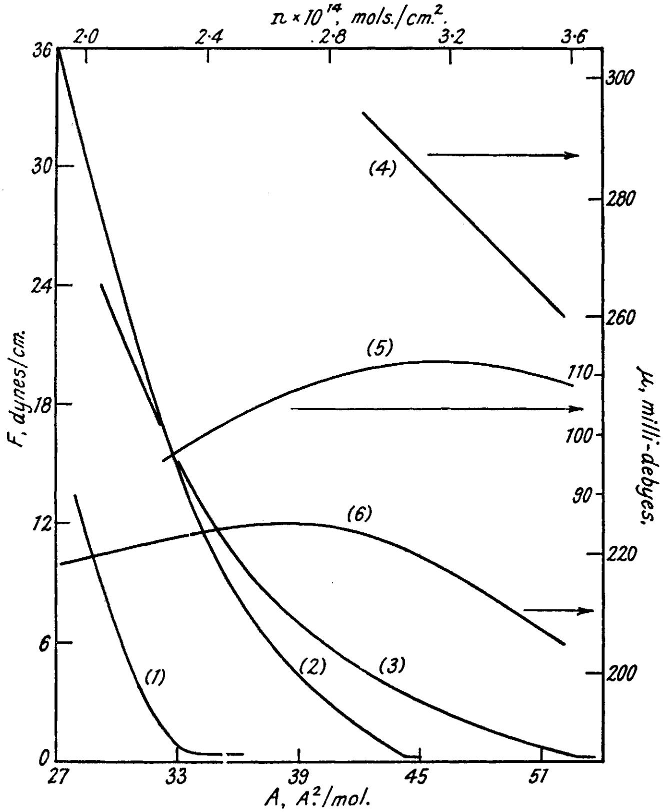


(IV.)

complete rigidity, so Zahn (*Trans. Faraday Soc.*, 1934, **30**, 804) and Sutton (*ibid.*, p. 789) suggested that it was due to resonance of the classical structure (III) with an excited one (IV), the C–O bond having in part the character of a double bond and so preventing the rotation. This has been confirmed by Sutton and Marsden (*loc. cit.*), and the associated energy barrier calculated to be of the order 5,500—7,500 cals./g.-mol.

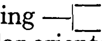


F–A and μ–n curves for films on 0·01N-*sulphuric acid at* 20—21°.

(1) *F–A, a-bromostearic acid.*	(4) *μ–n, a-bromostearic acid.*
(2) *F–A, a-triazopalmitic acid.*	(5) *μ–n, a-triazopalmitic acid.*
(3) *F–A, a-methylpalmitic acid.*	(6) *μ–n, a-methylpalmitic acid.*

The *F–A* and Δ*V–A* measurements for the various types of esters when spread as monolayers on water have been given in detail by Alexander and Schulman (*Proc. Roy. Soc.*, 1937, *A*, **161**, 115), who have shown that the configuration of the component dipoles in the ester group can be found with some accuracy from the values of the apparent moment. Six different configurations were identified in this way for esters of various types (from long-chain acid and short-chain alcohol, from short-chain acid and long-chain alcohol, and from long-chain acid and long-chain alcohol), and the structures were in agreement with the accessibility of the ester group as shown by its rate of hydrolysis on alkaline solutions.

A reference to these structures (Alexander and Schulman, *loc. cit.*, p. 125) shows that in the expanded films it was always the *cis*- and not the *trans*-form which appeared (*loc. cit.*, Table III, Figs. I and V), and in the condensed state either form was possible [cf. ethyl stearate and cetyl palmitate (*loc. cit.*, Table III, Figs. II and IV), which were *trans*, with octadecyl acetate and condensed cetyl propionate (*loc. cit.*, Table III, Figs. III and VI), which were *cis*]. Now the ester, despite its having been thrown on the surface in the *trans*-form (since the spreading solution was light petroleum), had been completely changed into the *cis*-form in the shortest time in which measurements could be taken ($\not>$20 secs.). This change, involving as it does rotation about the C–O bond, would suggest that the associated energy barrier is very small, certainly not more than a few hundred cals./g.-mol., as compared with the original value of some 5,500—7,500. This would agree with the value of *ca.* 400 cals./g.-mol. suggested by Sutton and Marsden (*loc. cit.*) for rotation about the C–O bond in the classical structure for the ester group. Hence, it would appear that immersion of the ester group in the polar aqueous medium has destroyed the resonance and with it the large associated energy barrier, since for long-chain esters at the air–water interface both *cis*- and *trans*-forms can exist, depending merely on the constitution of the ester and on the film pressure.

One very interesting application of this conclusion is in connexion with the structure of triglycerides in the solid state. From their *X*-ray and thermal investigation, Clarkson and Malkin (J., 1934, 666) concluded that in the crystal the central long chain is orientated in the opposite direction to the terminal ones, a simple representation being , but the great objection to this was, as they pointed out, the definitely known similar orientation of all three in monolayers (Adam, *Proc. Roy. Soc.*, 1922, *A*, **101**, 452). The discrepancy is readily explicable when models of the two orientations are examined (see *idem, ibid.*, p. 667), since these show that for the opposite alignment postulated in the crystal, all ester groups are in the *trans*-position, whereas similar orientation of the long chains requires the *central* one to be *cis* (in the most favourable configuration). The inference is obvious—in the crystal the energy barrier due to resonance permits only the *trans*-form and hence only opposite alignment, whereas on water, loss of resonance occurs, permitting easy transformation into the *cis*-form with all three chains aligned together.

The Triazo-group.—The diffraction of electrons by methyl azide vapour (Brockway and Pauling, *Proc. Nat. Acad. Sci.*, 1933, **19**, 860) could not be reconciled with the then generally accepted ring structure of the triazo-group, but indicated a linear structure with resonance between the forms $\text{—N}{=}\overset{+}{\text{N}}\overset{\rightarrow}{=}\overset{-}{\text{N}}$ and $\text{—}\overset{-}{\text{N}}\leftarrow\overset{+}{\text{N}}\equiv\text{N}$ [denoted in future by the (*a*) and the (*b*) form respectively], a view which was later confirmed by the *X*-ray measurements of crystalline cyanuric azide (Knaggs, *Proc. Roy. Soc.*, 1935, *A*, **150**, 576). Measurements on monolayers of α-triazopalmitic acid support the linear structure, and in addition indicate that in an aqueous medium resonance is no longer possible, the triazo-group existing solely in the (*b*) form.

The *F–A* and Δ*V–A* characteristics of α-triazopalmitic acid, $C_{14}H_{29}\cdot CH(N_3)\cdot CO_2H$, were determined by the usual methods on several aqueous substrates, and compared with those given by the closely related α-methylpalmitic * and α-bromostearic acids. The substrates employed were 0·01N-sulphuric acid, a phosphate buffer p_H 7·2 (Clark, "The Determination of Hydrogen Ions," 1928, p. 200), and tap-water (p_H 8·0, containing *ca.* 2×10^{-5} M-calcium as bicarbonate).

At p_H 2 the films were of the liquid-expanded type with a limiting area of 44 A.^{2} (at 21°), and could be compressed to about 27 A.^{2} ($F = 36$ dynes/cm.), whereat a slow collapse set in. The tap-water substrate gave a very similar behaviour, with a limiting area of 41 A.^{2} (*i.e.*, a slight condensation), but at p_H 7·2 the films were of the vapour-expanded type and were very much less stable. As measured by the movement of talc powder, the films were liquid at all compressions, even on the tap-water substrate. The figure, which gives the *F–A* curves of α-bromostearic and α-methyl- and α-triazo-palmitic acids obtained on

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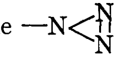
* This and other similar branched-chain acids are being studied by Dr. Stenhagen in this laboratory.

0·01N-sulphuric acid at room temperature (20—21°) shows that the α-triazo-compound (i) was easily the most stable of the three, despite its smaller chain length, (ii) could be compressed to smaller areas, (iii) had a smaller limiting area than the α-methyl compound (44 as against 53 A.^{2}), (iv) gave an extrapolated area at zero pressure of *ca.* 36 A.^{2} as compared with *ca.* 40 A.^{2} given by the α-methyl acid.

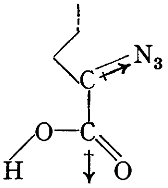
From the known parachors of compounds containing the triazo-, the bromo-, and the methyl group it is possible to compare approximately the cross-sections of these three radicals, it being assumed that they are spherical. Sugden (" The Parachor and Valency," 1930, p. 36) gives 55·8 for $—CH_3$ and 68·0 for —Br, and Lindemann and Thiele (*Ber.*, 1928, **61**, 1529) give 77·2 for $—N_3$. On the above assumption, their cross-sections should be proportional to 14·6, 16·7, and 18·2 respectively, *i.e.*, the effective cross-section of the triazo-group should be some 25% and 9% *greater* than the methyl- and the bromo-group respectively. Hence, for the analogous compounds α-methyl- and α-triazo-palmitic acids, the latter should have considerably the larger molecular area, whereas, in fact, the reverse was the case, the α-triazo-acid being compressible to even smaller areas than the α-bromostearic acid despite its shorter chain-length. Even if an abnormally high coefficient of compressibility be assumed for the  $—\mathrm{N}\!<\!\begin{smallmatrix}\mathrm{N}\\ \|\\ \mathrm{N}\end{smallmatrix}$ ring system, an assumption for which there seems no justification, the small molecular area occupied on the water surface requires some structure permitting a much closer packing. This condition can readily be seen from a model to be fulfilled by a linear structure of the three nitrogen atoms inclined at an angle of about 120° to the C·N bond. (Brockway and Pauling, *loc. cit.*, found a value of 135° ± 15° for this angle.)

The surface-potential measurements, which in the figure are given as the variation of the vertical component of the apparent dipole moment (μ) as a function of the surface concentration (n), provided further support for this linear structure. An examination of these μ–n curves revealed that (i) the moment of the α-methylpalmitic acid was practically identical with that of the unsubstituted acids (*ca.* 210 milli-Debyes), and after an initial small increase decreased on compression; (ii) the moment of the α-bromostearic acid was higher than that of the unsubstituted acid and *decreased* markedly on compression; (iii) the moment of α-triazopalmitic acid was only about one-half of that of the α-methyl or the unsubstituted acids, and *increased* by about 20% on compression.

The increase in apparent moment by the substitution of an α-bromine atom is readily explicable on the basis of a previously suggested configuration (Alexander, J., 1938, 729), but not so easily understood is the very pronounced effect in the opposite direction brought about by the α-triazo-group, since both produce a practically identical change in the dissociation constant of the n-fatty acids (cf. values of K_a : α-triazopropionic acid, $0{\cdot}9 \times 10^{-3}$; α-bromopropionic acid, $1{\cdot}1 \times 10^{-3}$; propionic acid, $1{\cdot}4 \times 10^{-5}$). On a p_H 7·2 substrate the moments were again very different, at an area of 36 A.^{2} that of the α-bromo-acid being 160 milli-Debyes and that of the α-triazo-acid 30, suggesting that the difference was due directly to the α-substituted groups and not at all to the carboxyl.

It has been shown by Sidgwick (" The Covalent Link in Chemistry," 1933, p. 195) that in non-polar solvents, whereas the moment of the $\mathrm{C}\overset{+}{\longrightarrow}\mathrm{N}_3$ link is about 1·5 D., yet the contribution from the links inside the N_3 group itself is very small, a fact which is explained by the resonance of the two linear forms (*a*) and (*b*) given above. Since the moment of the $\mathrm{C}\overset{+}{\longrightarrow}\mathrm{Br}$ link (1·6 D.) is practically identical both in magnitude and in direction with that of the $\mathrm{C}\overset{+}{\longrightarrow}\mathrm{N}_3$ link, very similar surface moments of the α-bromo- and the α-triazo-acid would have been expected, especially as their parachors do not differ much (see above). The pronounced difference found experimentally is much too great to be explicable on the basis of the $\mathrm{C}\overset{+}{\longrightarrow}\mathrm{N}_3$ moment alone, since several objections can be raised against the only possible structure which *might* possess such a low moment as 100 milli-Debyes at p_H 2. In such a structure (V) the decrease in the moment should be of the same magnitude as the increase brought about by the α-bromine substitution (*i.e.*, *ca.* 60 milli-Debyes), which is not nearly sufficient (the actual difference being *ca.* 110 milli-Debyes). In addition, and of more importance, is the fact that it involves the removal of the hydrophilic triazo-group from the substrate, and also the moment would be expected to *decrease* very rapidly on compression. The solution must therefore be sought in some internal change in the triazo-group itself, and the only plausible explanation seems to be that immersion of this group in the water has destroyed the resonance and caused it to revert to either the (*a*) or the (*b*) co-ordinated type. Such a loss of resonance brought about by immersion in an aqueous medium has previously been shown in the case of the ester group.

Reversion to type (*a*) being assumed, the configuration on the surface would undoubtedly be as shown in (VI), with the dipoles oriented as indicated. This configuration would, however, possess a very much *higher* moment than either the unsubstituted or the α-bromo-acid, on account of the presence of the co-ordinate link, which, in the *gas* phase, has a moment of at least 4 D. (Sidgwick, *Trans. Faraday Soc.*, 1934, **30**, 801). The experimental evidence definitely rules out this structure, leaving (*b*) as the only alternative, and suggesting that the surface structure is as shown in (VII). It is seen that this possesses the possibility of intramolecular electrostatic attractive forces between the carboxyl and the co-ordinated nitrogen atoms in the triazo-radical, which would tend to stabilise such a configuration. Squeezing the triazo- and the carboxyl groups together, as would occur on compression, can easily be seen to bring about an increase in the moment, although the total vertical moment will be less than in the unsubstituted acids. It is quite impossible to calculate the resultant vertical moment of this structure, since we have no knowledge of the moment of the $C{\cdot}N_3$ link or of those links in the triazo-radical when resonance is no longer possible, but a low value would be expected owing to the opposition between the carboxyl group and the co-ordinate link in the triazo-group.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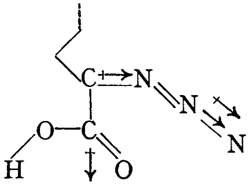
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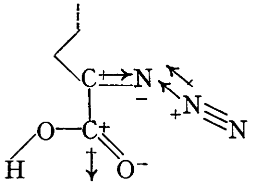
(VII.)

Sidgwick (*loc. cit.*, 1934) has attempted to calculate the energy of the two forms (*a*) and (*b*), the difference of which cannot be very great if resonance is possible, but the assumptions which have to be introduced make it impossible to state which is really the form with the lower energy. The fact that transition to the (*b*) form occurs in an aqueous medium does, however, definitely point to this as being the more stable form.

Considering all the arguments which have been put forward, it appears that these monolayer measurements upon α-triazopalmitic acid are completely incompatible with a ring structure for the triazo-group, but are in accord with a linear one having the structure $-\overset{-}{N}\leftarrow\overset{+}{N}\equiv N$. Hence it can be concluded that, in the case of the ester and the triazo-group which exist in a resonating form in non-polar solvents, immersion in water brings about a loss of resonance and reversion to one definite form : with the former to the classical structure (III), with practically completely free rotation about the C—O bond, and with the latter to the co-ordinated form $-N\leftarrow N\equiv N$.

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