238. *A Determination of the Structures of the Isomeric 2-Chlorovinyldichloroarsines.*

By C. A. McDowell, H. G. Emblem, and E. A. Moelwyn-Hughes.

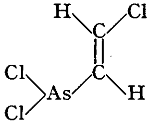
By measuring the dipole moments of the isomeric forms of 2-chlorovinyldichloroarsine in benzene solution, it has been established that ordinary " lewisite " is *trans*-2-chlorovinyldichloroarsine, while the new isomer isolated by Hewett (preceding paper) and termed " *iso*lewisite ", has the *cis*-configuration.

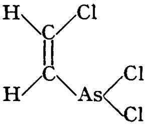
Classical stereochemical methods have generally been decisive in elucidating the configurations of optically active molecules, but they have not been so successful in cases of geometrical isomerism. Most of the purely chemical methods of attacking the latter type of problem depend on the assumption of *cis*- or *trans*-addition of reagents or elimination of groups, and it is only recently that evidence has been accumulated which shows that *trans*-addition and elimination are the processes which usually occur. In fact, even with this knowledge it is rarely possible to prove the configuration of *cis*- or *trans*-isomers by purely chemical methods alone. It is, however, often possible to supply strong supporting, and sometimes conclusive, evidence by the application of some of the techniques of physical chemistry.

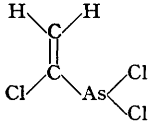
Of the various methods which might be used for this purpose, dipole-moment measurements are usually the easiest to carry out, and often give a unique answer. It is, in general, possible to estimate the probable dipole moment of a compound from its structure, by vectorial addition of the moments of the individual linkages. Comparison of this theoretical moment with the observed value shows whether or not the assumed structure is correct. This is the most satisfactory way of using dipole-moment measurements for structural determinations; but, in those cases of *cis–trans* isomerism where the groups in the molecule have approximately the same moment, it is often assumed that the compound with the larger moment is the one with the *cis*-configuration. In this way dipole moment measurements have helped to establish the configurations of the *cis*- and *trans*-isomers of the dihalogenoethylenes (Errera, *Compt. rend.*, 1926, **182**, 1623; *J. Phys. Radium*, 1925, **6**, 390; *Physikal. Z.*, 1926, **27**, 764), 2 : 2′-azoxytoluene and 2 : 2′-azoxyanisole (Müller, *Annalen*, 1932, **495**, 132), benzenediazocyanides (Le Fèvre and Vine, *J.*, 1938, 431), and azobenzene (Hartley and Le Fèvre, *J.*, 1939, 531); while similar measurements on the *O*- and *N*-methyl ethers of *p*-nitrobenzophenone oxime and the *O* ether of the corresponding aldoxime have enabled Sutton and Taylor (*J.*, 1931, 2190; Taylor and Sutton, *J.*, 1933, 63) to show that the Beckmann rearrangement takes place by a *trans*-interchange of the migrating groups.

Hewett (previous paper) has described the preparation of isomeric 2-chlorovinyldichloroarsines and the corresponding arsonic acids, and has shown that, though the two isomers have different physical and chemical properties, it is not possible by chemical evidence alone unambiguously to assign a configuration to either. On the basis of the available evidence it is assumed that the isomer which is formed in larger amounts, " lewisite ", has the *trans*-configuration (I), and that the other more volatile isomer, " *iso*lewisite ", has the *cis*-configuration (II). The main chemical difference between these two substances is their behaviour on treatment with cold dilute sodium hydroxide solution. Lewisite readily yields acetylene, whereas *iso*lewisite dissolves in the sodium hydroxide without evolution of gas, but on warming to 40° yields vinyl chloride.

With a view to obtaining more conclusive proof of the above assignments, and also to rule out the possibility that *iso*lewisite may be not a geometrical isomer, but the position isomer 1-chlorovinyldichloroarsine (III), we have measured the dipole moments of these substances in benzene at 25°.

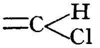

(I.)


(II.)


(III.)

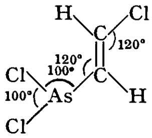
The dipole moment of lewisite was found to be $2{\cdot}20 \times 10^{-18}$ e.s.u. which is higher than the value 1·77 D. given by Möhler (*Helv. Chim. Acta*, 1938, **21**, 789). Möhler gives but few physical constants for the lewisite which he used, so we have no means of comparing the purity of our respective samples. It should be noted, however, that Möhler gives the electronic polarisation,

P_E, as 43·2 c.c. whereas the value calculated from our determinations of the density and refractive index of lewisite is 38·1 c.c. It should be pointed out that our values for the density and refractive index of lewisite are in very close agreement with the standard values for the vesicant as determined by the Chemical Defence Research Establishment. The difference in the two values for the dipole moment of lewisite is rather larger than is usually found for such measurements and must, therefore, be considered greater than the experimental error. At first it was thought that our lewisite was contaminated with some iodo-analogue, for, in its preparation, 2-chlorovinylarsonic acid is reduced with sulphur dioxide in the presence of a trace of iodine (Hewett, *loc. cit.*). An iodine-free sample was, therefore, obtained by carefully purifying crude lewisite prepared by the action of acetylene on arsenic trichloride in the presence of cuprous chloride (Jones *et al.*, *Ind. Eng. Chem.*, in the press); its dipole moment proved to be 2·23 D., in good agreement with that obtained for the previous sample. We have, therefore, adopted 2·21 D. as being the most reasonable value for the dipole moment of ordinary lewisite in benzene at 25°. The dipole moment of the *iso*lewisite isolated by Hewett (*loc. cit.*) was next measured under the same conditions and was found to be 2·61 D. The difference between the dipole moments of lewisite and *iso*lewisite, $\Delta\mu = 0·4$ D., is of the same order of magnitude as the difference in the moments of the *O*-methyl ethers of the *cis–trans* isomeric *p*-benzophenone oximes ($\Delta\mu = 0·51$ D., Taylor and Sutton, *loc. cit.*) and of the *O*-methyl ethers of similar isomeric *p*-benzaldoximes ($\Delta\mu = 0·49$ D., *idem, ibid.*). It thus seems reasonable to assume that lewisite is *trans*- and *iso*lewisite is *cis*-2-chlorovinyldichloroarsine. It has still, however, to be shown that *iso*lewisite is not 1-chlorovinyldichloroarsine. This possibility can be eliminated, and the evidence for the above assignments strengthened, by comparing the experimental values of the dipole moments with those calculated for structures (I), (II), and (III), from known, or estimated, contributions of the different linkages in these molecules.

The  $=\!C\!<^{H}_{Cl}$ group moment has been taken as being equal to the dipole moment of vinyl chloride, ~ 1·4 D., in benzene solution (the dipole moment of vinyl chloride in gas phase is 1·44 D. (Hugill, Coop, and Sutton, *Trans. Faraday Soc.*, 1938, **34**, 1518); and the C–As bond calculated from the dipole moment of $AsPh_3$ to be 1·07 D. (Bergmann and Schütz, *Z. physikal. Chem.*, 1932, *B*, **19**, 401). The moment of the $AsCl_2$ group was calculated from the dipole moment of arsenic trichloride, $\mu = 2·17$ D. (Smythe, *Proc. Roy. Soc.*, 1932, *A*, **136**, 256), knowing that this molecule is pyramidal with $\measuredangle$ Cl–As–Cl $\simeq$ 100° (Pauling and Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 2684); from these data we get $\mu_{AsCl_2} = 1·99$ D. Using these estimated contributions of the linkages and groups and the valency angles assumed in the following structures (Brockway, Beach, and Pauling, *ibid.*, p. 2693), Dr. L. E. Sutton has estimated, at our request, the values shown for the dipole moments of these compounds; he writes: " The theoretical values for the moments of these compounds, on the assumption that rotation of the asymmetrical polar groups about single bonds is completely free, were calculated by means of the formula

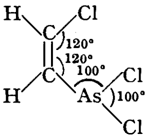
$$\bar{\mu}^2 = \mu_S{}^2 + \mu_R{}^2$$

where $\bar{\mu}$ is the average moment, μ_S is the resultant moment of all the non-rotating components, and μ_R is the rotating component (see Fuchs and Wolf, " Dielektrische Polarisation ", Leipzig, 1935, p. 397)."



(I*a*.)

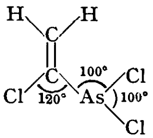
trans-2-Chlorovinyl-
dichloroarsine
$\mu_{calc.} = 2·03$ D.



(II*a*.)

cis-2-Chlorovinyldichloroarsine

$\mu_{calc.} \begin{cases} = 2·14 \text{ D. (no rotation of } AsCl_2 \text{ group)} \\ = 3·2 \text{ D. (free rotation of } AsCl_2 \text{ group)} \end{cases}$



(III*a*.)

1-Chlorovinyl-
dichloroarsine
$\mu_{calc.} = 1·15$ D.

On comparing these theoretical estimates with the experimentally determined values of the dipole moments of lewisite and *iso*lewisite we can immediately eliminate 1-chlorovinyldichloroarsine as a possible structure. Further, we see that the isomer with the smaller dipole moment is obviously *trans*-2-chlorovinyldichloroarsine whilst *iso*lewisite is *cis*-2-chlorovinyldichloroarsine. It will be noted that the experimentally observed dipole moment of *iso*lewisite lies between the values calculated for *cis*-2-chlorovinyldichloroarsine with and without free rotation of the $AsCl_2$ group, and is consistent with a hindered rotation. Considering the approximate nature of these estimations the agreement with experiment is very satisfactory and leaves little doubt that the assigned configurations are correct.

EXPERIMENTAL.

The experimental method and apparatus used have been described by Emblem and McDowell (*J.*, 1946, 641).

Materials.—Benzene. "AnalaR" Benzene was washed with concentrated sulphuric acid, dried over sodium, distilled, and frozen thrice to remove homologues. A sample was refluxed over phosphoric oxide for about 10 hours, stored over this reagent, and distilled from it immediately before use. It had $n_D^{20^\circ}$ 1·5010.

Lewisite. Two specimens of lewisite were used. Specimen *A* was prepared from the corresponding arsonic acid by reduction with sulphur dioxide in the presence of a trace of iodine (Hewett, *loc. cit.*), and had $n_D^{20^\circ}$ 1·6105, $d_{4^\circ}^{20^\circ}$ 1·8877. Specimen *B* was the specially prepared iodine-free lewisite obtained by purification of the plant product and had $n_D^{20^\circ}$ 1·6106, $d_{4^\circ}^{20^\circ}$ 1·8873.

iso*Lewisite.* This was a sample of the pure isomer prepared by Hewett (*loc. cit.*) and had $n_D^{20^\circ}$ 1·5888, $d_{4^\circ}^{20^\circ}$ 1·86827.

Results.—In the following tables ϵ = dielectric constant of the solution; w_1 = weight fraction of solute; d = density of solution; p_{12} = specific polarisation of solution; P_1 = molar polarisation of solute in benzene solution. The specific and molar polarisations were calculated by Sugden's method (*Trans. Faraday Soc.*, 1934, **30**, 722). All values are at 25°.

Molar polarisation of solutions of lewisite (specimen A) in benzene.

w_1.	d.	ϵ.	p_{12}.	P_1.
0·01565	0·8777	2·3087	0·34606	139·54
0·06307	0·9015	2·4513	0·36166	139·02
0·10160	0·9216	2·5710	0·37293	136·1
0·12326	0·9335	2·6464	0·37958	135·78

By graphical extrapolation of these data we get the molar polarisation at infinite dilution P_∞ = 140 c.c. From the refractive index and density of this specimen we get the electronic polarisation, P_E to be 38 c.c. Taking the atomic polarisation P_A to be 5% of P_E as suggested by Sugden and Groves (*J.*, 1937, 1779, 1782) we get P_{A+E} = 40 c.c.; hence, using the equation $P_\infty - P_{E+A} = P_O$, we get P_O, the orientation polarisation, to be 100 c.c.; this yields for the dipole moment of lewisite in benzene solution at 25° the value 2·20 × 10^{-18} e.s.u.

Molar polarisation of solutions of lewisite (specimen B) in benzene.

w_1.	d.	ϵ.	p_{12}.	P_1.
0·02368	0·8831	2·3368	0·34905	142·37
0·05115	0·8989	2·4247	0·35820	140·95
0·0688	0·9060	2·4750	0·36382	139·83
0·1451	0·9475	2·7268	0·38556	134·51

Graphical extrapolation of these data yields P_∞ = 143·2 c.c. Since P_{E+A} = 40 c.c., we get P_O = 103·2 c.c.; hence μ = 2·23 × 10^{-18} e.s.u. The agreement between these two values for the dipole moment of the two different specimens of lewisite is very satisfactory, and in this paper we shall adopt μ = 2·21 × 10^{-18} e.s.u. as being the best value for this constant at 25°.

Molar polarisation of solutions of iso*lewisite in benzene.*

w_1.	d.	ϵ.	p_{12}.	P_1.
0·04710	0·8948	2·4517	0·36445	174·49
0·0565	0·8997	2·4898	0·36882	173·24
0·06636	0·9052	2·5325	0·37351	172·68
0·1173	0·9329	2·7519	0·39519	166·69

From these data we obtain by graphical extrapolation P_∞ = 180 c.c. The refractive index and density of *iso*lewisite yield P_E = 37·4 c.c.; hence we take P_{E+A} as 39·28 c.c. This gives for P_O the value 140·72 c.c., from which we calculate the dipole moment, μ, of *iso*lewisite in benzene solution at 25° to be 2·61 × 10^{-18} e.s.u.

Pure specimens of lewisite and *iso*lewisite were prepared, respectively, by Dr. R. L. Barker and Dr. C. L. Hewett. We are indebted to Dr. L. E. Sutton for helpful advice and for permission to incorporate his theoretical estimates of the moments of the isomeric 2-chlorovinyldichloroarsines in this paper. Dr. G. H. Whiting kindly supplied information concerning the physical constants of both liquids. The work described here was carried out in the Chemical Defence Research Establishment of the Ministry of Supply, and is published with the consent of its Chief Scientist.

DEPARTMENT OF PHYSICAL AND INORGANIC CHEMISTRY,
THE UNIVERSITY, LIVERPOOL.
DEPARTMENT OF PHYSICAL CHEMISTRY,
THE UNIVERSITY, CAMBRIDGE.

[*Received, May 28th,* 1947.]