ally more stable than six-membered rings when the ring contains no double bonds.

An apparent exception to the foregoing examples of increased aquation rate with increased crowding is the case of the 1,3-diamino-2,2-dimethylpropane complex (no. 12 in Table I). A comparison with the trimethylenediamine complex shows that in this case the rate is actually lessened as a result of adding methyl groups to the bidentate chain. There seems to be no simple explanation as to why methyl substitution on a six-membered chelate ring decreases the rate of aquation while methyl substitution on a five-membered ring increases the rate of aquation.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY OF THE UNIVERSITY OF CALIFORNIA]

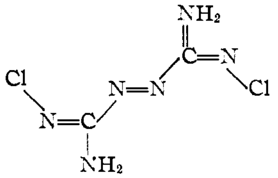
The Dipole Moments, Ultraviolet Spectra and Structure of Azo-bis-(chloroformamidine) and Azo-bis-(nitroformamidine)

BY W. D. KUMLER

RECEIVED FEBRUARY 7, 1953

Azo-bis-(chloroformamidine) has a dipole moment of 1.95 *D* and azo-bis-(nitroformamidine) a moment of 3.63 *D*. The comparatively low moments considering the size of the individual group moments making up the molecules suggest the compounds have the *trans* configuration about the N=N double bond. The chloro compound with a λ_{max} 345, ϵ_{max} 14,700 absorbs at longer wave length and with higher extinction than the nitro compound λ_{max} 312, ϵ_{max} 5840. The imine structures are capable of accounting for the behavior. A consideration of the properties of the ion produced by the removal of a proton from either the chloroimine or chloroamine structure suggests the molecule has the chloroimine structure. The same reasoning applies to the nitro compound.

The problem of structure in these molecules is concerned mainly with whether they are *cis* or *trans* with respect to the azo linkage and whether the chlorine atoms and the nitro groups are attached to a singly or doubly bonded nitrogen atom. The two *trans* structures for the chlorine compound are represented by structures (1) and (2).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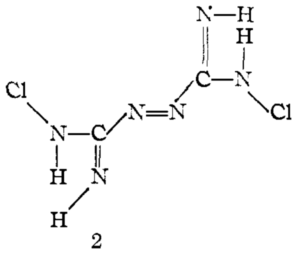
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The dipole moments of the compounds were measured in dioxane at 30°. The dioxane was purified as before.[1] The compounds were highly purified samples supplied to us by Professor George F. Wright. The dipole moments were calculated using the equation and method of Halverstadt and Kumler.[2]

$$p_{2_0} = \frac{3\alpha\nu_1}{(\epsilon_1 + 2)^2} + (\nu_1 + \beta)\,\frac{\epsilon_1 - 1}{\epsilon_1 + 2}$$

$$P_{2_0} = p_{2_0}\,M_2$$

$$\mu = 0.01281\,\sqrt{(P_{2_0} - P_{E_2})T}$$

ϵ_1 and ν_1 were obtained by extrapolating the straight line ϵ_{12}–ω_2 and ν_{12}–ω_2 curves to zero concentration.

Azo-bis-(chloroformamidine)

ω_2	ϵ_{12}	ν_{12}
0.000400	2.2063	0.97375
.000577	2.2067	.97365
.000794	2.2072	.97357
.000975	2.2081	.97344
.001193	2.2087	.97335

ϵ_1	α	ν_1	β	P_{2_0}	P_{E_2}	μ
2.2050	3.00	0.97393	−0.48	116.6	40.4	1.95

Azo-bis-(nitroformamidine)

ω_2	ϵ_{12}	ν_{12}
0.000189	2.2076	0.97374
.000312	2.2089	.97366
.000429	2.2102	.97360
.000536	2.2107	.97353
.000805	2.2128	.97334

ϵ_1	α	ν_1	β	P_{2_0}	P_{E_0}	μ
2.2062	8.37	0.97385	−0.59	306.6	41.6	3.63

The comparatively low moments of both of these compounds considering the moments of the individual groups that make them up suggest that the compounds have the *trans* and not the *cis* configuration. A *cis* structure would enable the groups to augment one another so the expected moment would be considerably larger than the observed moment. On the other hand, the *trans* structure allows enough opposition so that the observed moments are reasonable for such a configuration.

The dipole moments do not enable a decision to be made with regard to whether the chlorine and nitro groups are attached to singly or doubly bonded nitrogen atoms. The ultraviolet spectra of the compounds, however, shed some light on this question. The chlorine compound with λ_{max} 345 and ϵ_{max} 14,700 absorbs at considerably longer wave length and with higher extinction than the nitro compound with λ_{max} 312 and ϵ_{max} 5,840. It is unusual for corresponding nitro and chlorine compounds to act in this manner, for the reverse is the usual behavior, namely, that the nitro compound absorbs at longer wave lengths and with higher extinction. For example nitrobenzene absorbs at longer wave lengths and with higher extinction than chlorobenzene. The behavior of these azo compounds can be accounted for in the following way. If the chlorine compound has structure (1), then resonat-

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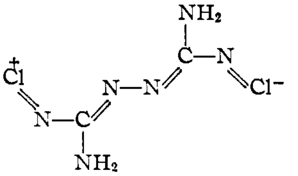
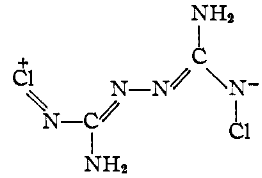
[1] W. D. Kumler and I. F. Halverstadt, THIS JOURNAL, **63**, 2182 (1941).

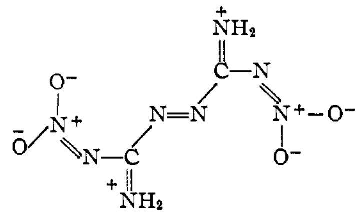
[2] I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).

ing forms involving conjugation clear across the molecule are possible.



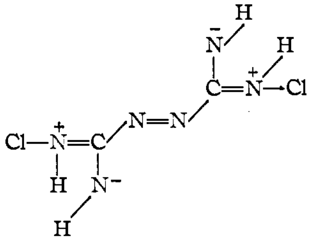


Such a situation is not present with the nitro compound for here only local conjugation is possible and the central double bond is still present in the form with a separation of charge.



Thus the chlorine compound should have a low lying excited state of more stability than the nitro compound and consequently absorb at longer wave length and with greater extinction.

With structure (2), it is not possible to write forms with a separation of charge involving oscillations clear across the molecule

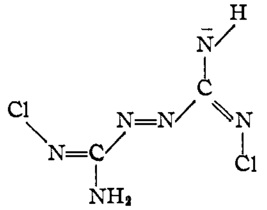


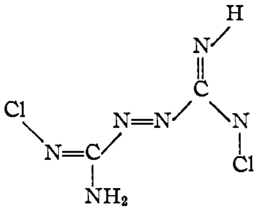
3

and so this structure does not account for the observed ultraviolet spectra. Structure (3) simply changes the position of the double bonds at the ends of the conjugated system in (2) so that there would be no long oscillations in going from (2) to (3) and hence the absorption would be at relatively short wave lengths.

The spectra then suggest the compounds have structure (1) with the chlorine and nitro groups attached to doubly bonded nitrogen atoms.

Another way of considering this problem is to suppose a proton dissociates from either structure (1) or structure (2). The resulting ion in either case is the same resonance hybrid.





When a proton returns to this ion two different molecules can be formed depending on to which nitrogen it returns. It will go to the nitrogen of greatest basicity which is expected to be the one to which the hydrogen is attached rather than the one to which the much more electronegative chlorine atom is attached. On the basis of this reasoning, the structure of the compound should be (1) and not (2). The same reasoning also favors the similar nitrimine structure for the nitro compound. This method of approach is thus in agreement with the deductions from the ultraviolet spectra that the compounds are chloroimines and nitrimines. The dipole moment data suggest the azo linkage is *trans*.

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[CONTRIBUTION FROM LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA]

Permeability and Solubility of He^3 and He^4 in Vitreous Silica[1]

BY W. M. JONES

RECEIVED MARCH 5, 1953

The relative permeabilities and solubilities of He^3 and He^4 in vitreous silica have been measured as a function of temperature, and the differences in the diffusion activation energies and heats of solution evaluated. The absolute permeabilities and solubilities also were obtained.

I. Relative Permeabilities and Solubilities

Introduction.—It was considered of interest to measure the relative permeabilities and solubilities of He^3 and He^4 in vitreous silica at several temperatures, particularly with regard to a possible small difference in diffusion activation energies and its relationship to the theory of rate processes.

Apparatus and Materials.—The main features of the permeability apparatus used at the five highest temperatures are given in Fig. 1. The He^3–He^4 mixture was contained inside the hollow sphere A communicating with an input measuring and transfer system through the 0.7-mm. bore capillary D. Gas diffused from the sphere into the space C, from which it was frequently transferred through F to a second measuring system. The seal E at room temperature was made with Armstrong cement. Copper-wool between A and B was found by differential thermocouple measurements to bring A to the temperature of the surrounding bath. The stirred bath of silicone fluid or of fused lithium, sodium and potassium nitrates in eutectic proportions was regulated to ±0.05° or better. Temperatures were measured with a NBS calibrated platinum resistance thermometer which was protected from the bath with a thin, close-fitting platinum sheath. At 0° a crushed ice-bath was used. The apparatus used at 356.8 and 273.16°K. was similar to that in Fig. 1, except that the collection jacket was Pyrex and its connection to the capillary D was made a short distance above the sphere with a graded seal. The spheres were prepared from clear fused quartz. Volume, weight, density and micrometer measurements were made. The spheres were about 3.8 cm. o.d. The average wall thickness of the sphere at the lowest two temperatures

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[1] This work was sponsored by the A.E.C.