

### Emission of Molecular Complexes of Nitro-compounds

Lewis and Kasha<sup>1</sup> have directed attention to the phosphorescence induced by ultra-violet light on a number of organic compounds, particularly nitro-compounds, dissolved in the 'glass' produced when their solutions in suitable solvent mixtures are cooled to liquid-air temperature. They attribute this phenomenon to the formation of triplet-levels from the original excited singlets, the phosphorescence resulting from the triplet-ground-level change being unquenched owing to the greatly diminished thermal agitation at low temperatures in the glass.

We have found that even at ordinary temperatures an intense brick-red fluorescence is produced in ultra-violet light when an acetone solution of *s*-trinitrobenzene is shaken with a few crystals of potassium cyanide. In a mixture of methyl and ethyl alcohols (1:5), the fluorescence is orange-red; when this is frozen to a glass in liquid air, it exhibits a short-lived orange phosphorescence (with very dilute solutions the phosphorescence is green). We have examined other systems, not all of which show fluorescence at ordinary temperatures, but all of which emit radiations at liquid-air temperature. Our preliminary observations are recorded in the accompanying table.

In solution in methanol/ethanol (1:5)	Fluorescent colour at room temperature	Phosphorescent colour at liquid-air temperature
Sodium nitrite/sym-trinitrobenzene	—	blue
" /chloranil	—	blue
" cyanide/ <i>o</i> -dinitrobenzene	green	blue-green
" " / <i>m</i> - "	green	pale-blue
" " / <i>p</i> - "	greenish-brown	—
" " /sym-trinitrotoluene	—	green
" " /chloranil	green	red (green on dilution)
" acetate/sym-trinitrobenzene	orange-red	blue
Methylamine/sym-trinitrobenzene	red	yellow-green
		orange

We believe that in these systems there is immediate complex formation, involving some donor-acceptor mechanism whereby a transition between molecular levels, originally forbidden, becomes permitted in the complex. Whether this level, distorted by the proximity of the donor molecule, corresponds to a level in the acceptor molecule or its ion, we cannot at present say.

We are grateful to Dr. E. J. Bowen for his suggestions and discussion.

*Note added in proof.* It may be mentioned that, since this letter was submitted, Reid<sup>2</sup> has described the emission spectra of certain hydrocarbon - aromatic nitrocompound complexes. He arrives at similar conclusions concerning the nature of the transitions involved.

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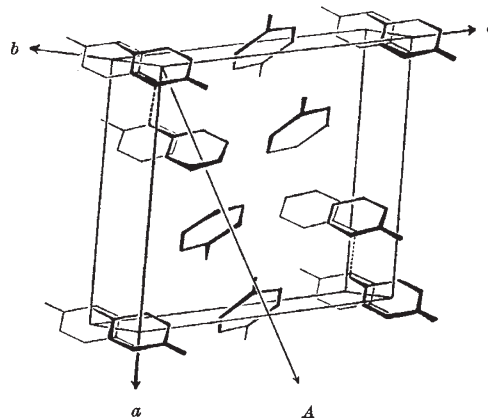
<sup>1</sup> Lewis and Kasha, *J. Amer. Chem. Soc.*, **66**, 2100 (1944).

<sup>2</sup> Reid, *J. Chem. Phys.*, **20**, 1212, 1214 (1952).

### Molecular Compounds of the Quinhydrone Type

THE nature of the molecular interaction in the formation of crystalline quinhydrone has been discussed previously by Anderson<sup>1</sup>. By comparison of preliminary crystallographic data for a number of quinhydrone, he came to the conclusion that the molecules are held together by the interaction of polar groups and polarizable aromatic substances, and that hydrogen-bond formation is not an essential structural feature, though it is not necessarily excluded. We have now been able to confirm these conclusions by a detailed structure determination of phenoquinone (which will be reported in full elsewhere), and by comparison with further preliminary data for quinhydrone and other molecular compounds of this type.

The arrangement of molecules in the unit cell of phenoquinone is shown in the accompanying diagram. Each quinone molecule, such as that at 000, is sandwiched between a pair of centrosymmetrically related phenol molecules, for example, those at  $\frac{1}{2} 0 \frac{1}{2}$  and  $\frac{3}{2} 0 \frac{1}{2}$ . This results in the structure being built up of sets of three molecules arranged in columns parallel to the direction marked *A* in the diagram. In each set the plane of the quinone molecule is parallel to those of its two adjacent phenol molecules and is separated from them by a distance of 3.33 Å. Each phenolic hydroxyl group forms a hydrogen-bond of length 2.64 Å. with a quinone molecule in an adjacent column, two such hydrogen-bonds being indicated in the diagram by broken lines.



In order to compare this structure with that of quinhydrone, we must take into consideration the fact that, in the latter structure, the molecules must lie in special positions, since there are only two of each type of molecule in a cell of space-group  $P2_1/c$ . Further, on X-ray photographs taken with the crystal oscillating about its *a*-axis, the extremely low intensity of reflexions on layer lines of odd order indicates an almost exact repetition of the structure at intervals of  $a/2$  parallel to the *a*-axis. The only choice of special positions which makes this arrangement possible necessitates the stacking of quinone and quinol molecules alternately, in continuous columns along the *a*-axis. This means that the unit cell of quinhydrone must be compared with the cell formed by the *A*-, *b*- and *c*-axes of phenoquinone as shown below.