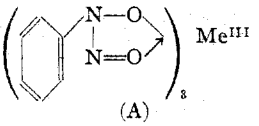
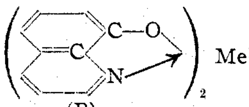
compounds with metal ions, it was found advisable to devise a system for the classification of chelating groups present in various organic compounds to serve as a basis of comparison. The available classifications, in particular that of Diehl,[1] are too unwieldy for rapid grouping and comparison. In addition to classifying the organic compounds now known, any system should also present information concerning possible reagents. The common method of indicating the number of members in the completed chelate ring is too cumbersome, in view of the recent increases in both number and variety of compounds possessing groups capable of chelation.

TABLE I

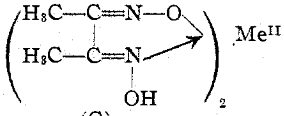
Group designation	Representative compound
C-N, SH	Mercaptobenzothiazole
C-NH, SH	Rubianic acid
C-NOH, OH	Benzohydroxamic acid
N-NONH$_4$, O	Cupferron (A)
C,C-N, NOH	Phenyl α-pyridyl ketoxime
C,C-N, OH	8-Quinolinol (B)
C,C-N, SH	8-Quinolinethiol
C,C-NH, SH	Thionalide
C,C-NH$_2$, OH	Glycocoll
C,C-NOH, NOH	Dimethylglyoxime (C)
C,C-NOH, O	α-Nitroso-β-naphthol
C,C-O, OH	Oxalic acid
C,C-O, SH	Thioglycolic acid
C,C-OH, OH	Catechol
C,C-OH, S	Thiohydantoic acid
C,N-NH, NOH	Nitrosoguanidine
C,N-NH$_2$, OH	Hydrazinecarboxylic acid
C,N-NH$_2$, SH	Dithizone (D)
C,C,C-N, NH	Chlorophyll type
C,C,C-NOH, OH	Salicylaldoxime (E)
C,C,C-O, OH	Alizarin
C,C,N-N, NH	Phthalocyanine
C,C,N-NH, NH	Biguanidine
C,C,N-NH, NH$_2$	Biuret
C,C,N-NH, O	Dicyandiamidine (F)



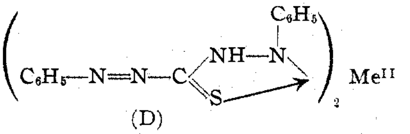
(A)



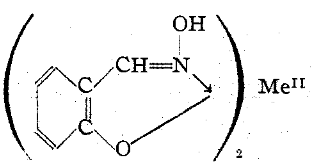
(B)



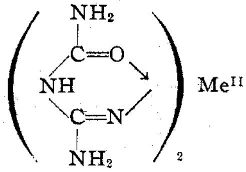
(C)



(D)



(E)



(F)

In this classification the two functioning groups, which supply the primary and secondary valences involved in the general formation of a chelate ring, and the atom or atoms linking these two groups form the basis of the system. Compounds with identical chelating groups have the same group designation, regardless of the structure of the remainder of the molecule. The group designation is derived as follows: (*a*) The atom or atoms connecting the two functional groups are expressed by their conventional symbols, arranged alphabetically. (*b*) The functioning groups are given by their symbolic representations in alphabetical order of the atoms by which they are attached to the original compound before chelation.

In salicylaldoxime, for example, the functional groups are linked by three carbon atoms, and these functional groups are the oxime and hydroxyl radicals. Consequently, the classification is C,C,C-NOH, OH.

The accompanying list gives in order of increasing complexity the designations of the more common chelating groups and the names of representative compounds containing such groupings. For the sake of clarity, structural formulas illustrating some of the inner complexes formed are also given. It is evident that exact knowledge of the structure of the chelate compound formed is not essential for this method, insofar as the primary and secondary valence connections are concerned. No attempt is made to designate these linkages as to type, and compounds are arranged solely on the basis of general structure.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON

RECEIVED JULY 29, 1938

---

[1] H. Diehl, *Chem. Rev.*, **21**, 39–111 (1937).

Dynamic Isomerism of Acetaldehyde 2,4-Dinitrophenylhydrazone

BY W. M. D. BRYANT

In earlier papers the writer[1,2] presented conclusive evidence based on optical crystallographic measurements that there are at least two distinct crystalline modifications of acetaldehyde 2,4-

---

[1] Bryant, THIS JOURNAL, **55**, 3201 (1933).

[2] *Ibid.*, **58**, 2335 (1936).

dinitrophenylhydrazone, and refuted the contention of Campbell[3] that the second modification is merely a product contaminated with the dinitrophenylhydrazone of another carbonyl compound. On the basis of the evidence then available the relationship between these two crystal modifications was assumed to be one of polymorphism. However, a new melting point study using a Kofler and Hilbck micro heating stage[4] has been completed and the results indicate dynamic isomerism rather than polymorphism as the true relationship. This explanation was proposed by Allen and Richmond[5] on the basis of some work by Bredereck[6] with substituted furfural derivatives, and is in accord with the new experimental results.

Experimental

The new melting point observations were made using a Kofler and Hilbck micro heating stage[7] mounted on the object stage of a chemical microscope equipped with a 10X Reichert heat resisting objective. By this means thermal changes in individual crystals could be followed and the temperatures read by means of a calibrated thermocouple. Melting points by this method were found accurate to ±2° and precise to ±0.5°. The samples of acetaldehyde 2,4-dinitrophenylhydrazone employed were prepared during the two earlier investigations.

Acetaldehyde 2,4-dinitrophenylhydrazone I (previously called the "stable form") recrystallized five times from 95% ethanol[1] was found to melt sharply without transition at 168–170° in agreement with 168.5° obtained previously by the more precise macro method. Above 115° in the initial heating a slight sublimate of orange lozenge-shaped crystals appeared and was recognized as the II modification (previously designated as "metastable"). These crystals melted at 156–157°. A few of these crystals in contact with modification I began melting at slightly lower temperature. The resulting liquid noticeably eroded plates of the I form below their regular melting temperature. In another experiment the sublimate was the I form (plates) and melted at the higher temperature (168–170°). On slowly cooling the liquid phase after complete fusion, the II form often reappeared first, usually at 130–140°; on reheating, this form was in equilibrium with the liquid at 148°, a slight change of temperature being sufficient to induce either growth or solution. In cases where the I form reappears first, the fusion or solution process begins at 150–155° and complete solution occurs between 155 and 160°. The above behavior is typical of a system in which the two compounds are, strictly speaking, different chemical entities but mutually convertible one into the other.

A sample of derivative recrystallized once from benzene[2] had an initial melting point of 148–151°. Crystals (mainly the II modification) reappeared at 131° and were completely fused (or dissolved) at 149.5°. After several repetitions the fusion temperature was lowered to 142°.

The above observations indicate that acetaldehyde 2,4-dinitrophenylhydrazone exists in two chemically different forms (dynamic isomers), the ordinary form (I) melting sharply near 169° and a form (II) obtained by sublimation melting at 157°. Crystallization of the melt produces a mixture (probably an equilibrium mixture) melting near 148°. The derivative recrystallized from benzene although optically identical with the I modification melts near 149° as does the "equilibrium mixture," hence must contain traces of a catalyst (possibly sulfuric acid) capable of inducing a rapid isomerization. This accounts for the low melting points sometimes observed.[2] In the writer's earlier experiments[1] slow isomerization was mistaken for a more fundamental thermal breakdown and hence not given the attention it deserved.

AMMONIA DEPARTMENT
E. I. DU PONT DE NEMOURS & CO., INC.
WILMINGTON, DELAWARE

RECEIVED OCTOBER 3, 1938

Structure of Lignin

BY M. J. HUNTER, A. B. CRAMER AND HAROLD HIBBERT

In a recent note[1] the isolation of an aromatic ketone, $C_{13}H_{18}O_4$, from spruce wood by organic solvent extraction was reported and the additional presence of derivatives containing the syringyl group from hard woods noted.

Using maple wood and similar organic solvent extraction, there is obtained a mixture of two ketones, having in the pure state the empirical formulas $C_{12}H_{16}O_4$ and $C_{13}H_{18}O_5$, respectively, which can be readily separated by conversion into their *p*-nitrobenzoates.

One of these corresponds to the ester from the ketone previously reported, while the new crystalline *p*-nitrobenzoate is derived from the second ketone, the latter being related to the former by possessing an additional methoxyl group. They are apparently present in approximately equal amounts.

The theoretical conclusion drawn previously that hard woods differ from soft in having present in the building unit not only the guaiacyl but also the syringyl radical has thus been substantiated.

---

[3] Campbell, *Analyst*, **61**, 391 (1936).

[4] Kofler and Hilbck, *Mikrochemie*, **9**, 38 (1931).

[5] Allen and Richmond, *J. Org. Chem.*, **2**, 222 (1937).

[6] Bredereck, *Ber.*, **65**, 1833 (1932).

[7] This instrument manufactured by the optical firm of C. Reichert, Vienna, was obtained from Pfaltz and Bauer, Inc., Empire State Building, New York City.

[1] THIS JOURNAL, **60**, 2274 (1938).