product showed exactly the same slender needle form and melting point as 2,5-diphenylthiohydroquinone diacetate. The identity was confirmed by a mixed melting point.

In a similar way the β-form was also reduced to 2,5-diphenylthiohydroquinone.

Summary

The meso and racemic forms of 2,5-diphenylsulfinylhydroquinone have been isolated. These represent a pair of diastereoisomers in the class of di-diarylsulfoxides.

URBANA, ILLINOIS

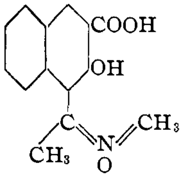
RECEIVED JULY 24, 1933
PUBLISHED NOVEMBER 7, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

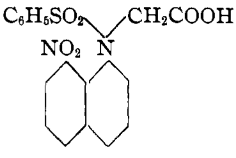
Study of Certain Analogs of Resolvable Diphenyls

BY MARION E. MACLEAN[1] AND ROGER ADAMS

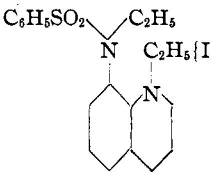
The cause of optical activity in properly substituted diphenyls is now generally ascribed to restricted rotation of the two rings.[2] Meisenheimer[3] has observed in certain substituted oximes (I) and Mills[4] in certain nitronaphthalenes (II) and quinoline derivatives (III), optical isomerism which may also be explained on the basis of restricted rotation due to the interference of groups.



I



II



III

Similar possibilities[5] in substituted aryl aliphatic compounds have been suggested but none have as yet been prepared in which resolution has been realized.

It is clear from the work cited above that other cases of optical activity caused by interference of adjacent groups are to be anticipated. Compounds related to the diphenyl series of the general structure indicated in IV, V and VI have now been investigated.

From experience in the diphenyl series, the methyl group may be assumed to be relatively large.[2] Consequently, if (a) in the above formulas represents a methyl group, the 2,2′ groups in these molecules should pro-

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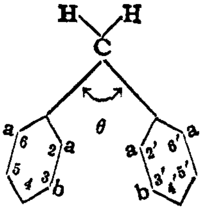
[1] Submitted as part of a thesis for the degree of Doctor of Philosophy at the University of Illinois. The junior author held during 1931–1932 the Julia C. G. Piatt Memorial Fellowship of the A. A. U. W. She desires to express her thanks for this aid.

[2] Adams and Yuan, *Chem. Rev.*, **12**, 261 (1933).

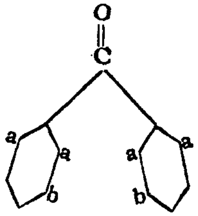
[3] Meisenheimer, Theilacker and Beisswenger, *Ann.*, **495**, 249 (1932).

[4] Mills, *Trans. Faraday Soc.*, **26**, 431 (1930); Mills and Breckenridge, *J. Chem. Soc.*, 2209 (1932); Mills and Elliott, *ibid.*, 1291 (1928).

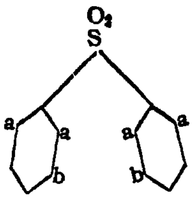
[5] Hyde and Adams, THIS JOURNAL, **50**, 2499 (1928); Maxwell and Adams, *ibid.*, **52**, 2959 (1930).



IV



V



VI

duce a pronounced interference and thus lead to non-coplanar rings which would make possible optical isomerism, provided (1) that the angle θ which in an undistorted carbon atom is 109° 28′ is not materially modified by the substituent groups and (2) that the two rings during rotation on the methylene groups are not so synchronized as to slip by each other.

Strong evidence that the valence angles of a carbon atom vary with the character of the atoms or groups attached has been offered by Ingold,[6] Thorpe and others.

Dipole moment measurements have also indicated in some instances spreading of the valence angles. The very small moment of diphenylmethane[7] led to the conclusion that the axes of the two phenyl groups are very nearly in a straight line. In benzophenone and its *p*-substituted products, the angle between the single valencies has been found to be about 130°.[8] For diphenyl sulfone, however, the valence angles of sulfur have been calculated as practically 109°.[9] It is possible that in the dimesityl compounds the deformation would be greater than in the corresponding diphenylmethane derivatives.

From these data it might be predicted that in dimesitylmethane and dimesityl ketone, the methane carbon would be so distorted that the 2,2′-methyl groups would interfere only slightly if at all and restricted rotation with consequent optical activity might not result. Restricted rotation would seem more likely in the case of dimesitylsulfone, although the length of the carbon-to-sulfur linkage might be enough greater than the carbon-to-methylene linkage to govern to some extent the possibility of interference between the methyl groups.

A compound of each type mentioned above has been prepared, 3,3′-diaminodimesitylmethane (VII), 3,3′-diaminodimesityl ketone (VIII) and 3,3′-diaminodimesityl sulfone (IX).

Each compound yielded a crystalline di-camphor sulfonate and di-bromocamphor sulfonate, but these on fractional crystallization gave no evidence of separation into diastereoisomers and on decomposition with ammonia

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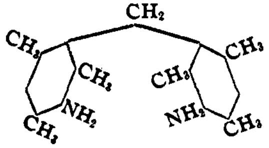
(6) Ingold, *J. Chem. Soc.*, **119**, 305 (1921), and subsequent papers by the same author and his co-workers.

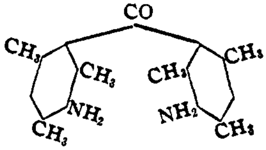
(7) Estermann, *Z. physik. Chem.*, **B1**, 161 (1928).

(8) Bergmann, Engel and Meyer, *Ber.*, **65**, 446 (1932).

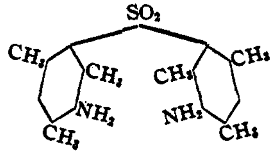
(9) Bergmann and Tschudnowsky, *ibid.*, **65**, 457 (1932).



VII



VIII



IX

at 0°, each salt yielded an inactive amino compound. No mutarotation of the salts was observed even at 0°. This failure to demonstrate the presence of enantiomorphs in the three diamino compounds suggests a distortion of the tetrahedral structure of the sulfur and of the methane carbon atoms in these compounds to a degree which permits free rotation of the mesityl groups or perhaps a synchronizing of the rings during rotation, or even both.

Experimental

Dimesityl ketone was prepared either by the action of carbon monoxide on mesitylene under pressure in the presence of aluminum chloride[10] or by the condensation of 2,4,6-trimethylbenzoyl chloride and mesitylene. Upon nitration and reduction, VIII was obtained. To prove that nitration did not yield a 3,5-dinitro instead of a 3,3′-dinitro derivative, 3,5-dinitromesityl mesityl ketone was prepared from 3,5-dinitro-2,4,6-trimethylbenzoyl chloride and mesitylene and was shown not to be identical with the nitration product of dimesityl ketone.

3,3′-Diaminodimesitylmethane was obtained by a Clemmensen reduction of the dinitrodimesityl ketone. Attempts to nitrate dimesitylmethane prepared from formaldehyde and mesitylene proved unsuccessful.

Diaminodimesityl sulfone was obtained by nitration and reduction of dimesityl sulfone. By analogy to the ketone, it was assumed that the nitro groups entered one in each ring.

Dimesityl Sulfone.—A mixture of 147 g. of mesitylene sulfonyl chloride,[11] 100 g. of mesitylene and 1 liter of carbon disulfide was placed in a three-necked, 1-liter, round-bottomed flask fitted with a reflux condenser protected by a drying tube and 100 g. of aluminum chloride was added, causing an immediate mild reaction. Refluxing on a water-bath was maintained for eleven hours. The carbon disulfide was distilled off and the contents of the flask poured out onto ice. The product, after filtering and drying, weighed 153 g. (75%). Purification is best accomplished by crystallization from glacial acetic acid, m. p. 202–204° (corr.). This substance has been described previously by Meyer,[12] who reported m. p. 195° but gave no details for the preparation.

3,3′-Dinitrodimesityl Sulfone.—A mixture of 9.5 g. of dimesitylsulfone and 1 liter of concentrated nitric acid (sp. gr. 1.42) was heated in an open, round-bottomed flask on the steam-bath for five hours. The dimesitylsulfone dissolved to a pale yellow solution. Upon cooling, 9 g. of very pale yellow crystals separated and more could be re-

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[10] Krase and Macmillan prepared this product by the high pressure reaction and kindly furnished a sample for part of the experiments described in this investigation.

[11] Demény, *Rec. trav. chim.*, **50**, 51 (1931).

[12] Meyer, *Ann.*, **433**, 327 (1923).

covered by diluting the filtrate, m. p. 172–174° (corr.). This proved to be the pure product. Less pure portions were recrystallized from glacial acetic acid.

Anal. Calcd. for $C_{18}H_{20}N_2O_6S$: N, 7.14. Found: N, 7.37, 7.30.

3,3'-Diaminodimesityl Sulfone.—A mixture of 17.2 g. of crude 3,3'-dinitrodimesityl sulfone, 500 cc. of glacial acetic acid, 150 cc. of water and 35 cc. of concentrated hydrochloric acid in a three-necked flask provided with a mercury-sealed stirrer and a reflux condenser was heated on a steam cone for a short time until the solid had dissolved completely. Powdered zinc was added in portions, 90 g. in all, and 20 cc. of water with 15 cc. of concentrated hydrochloric acid was also added after a time. The heating was continued for about nineteen hours.

After filtration, the amine was precipitated from the acetic acid solution, previously cooled and diluted with ice, by addition of excess ammonia. It was further purified by redissolving in warm dilute hydrochloric acid and reprecipitating with ammonia (yield 13.2 g., 91%). After one recrystallization from glacial acetic acid and one from alcohol the needles had a m. p. of 217.5–218.5° (corr.).

Anal. Calcd. for $C_{18}H_{24}N_2O_2S$: C, 65.02; H, 7.28; N, 8.43. Found: C, 65.31; H, 7.63; N, 8.51.

Dimesityl Ketone.—This product was made by the Friedel and Crafts reaction as described by Kohler and Baltzly.[13] It had the same melting point as that obtained by the action of carbon dioxide on mesitylene.[10]

3,3'-Dinitrodimesityl Ketone.—A solution of 70.5 g. of crude dimesityl ketone in a liter of concentrated sulfuric acid was cooled to −14.5°. Then 35.5 g. of nitric acid (sp. gr. 1.5) in 250 cc. of concentrated sulfuric acid, also previously cooled in an ice-salt bath, was added slowly with mechanical stirring over a period of two hours. The temperature did not rise above −9.5° during the addition but remained below −10° nearly the entire time. Stirring was continued and the solution was left standing for three hours, the temperature rising nearly to 0°. Then the liquid was poured very slowly, with vigorous stirring, onto ice; yield, 89 g. (95%). The nearly white, granular crystals were purified by recrystallization from alcohol, m. p. 171.5–172.5° (corr.).

Anal. Calcd. for $C_{19}H_{20}N_2O_5$: C, 64.01; H, 5.66; N, 7.86. Found: C, 64.15; H, 5.77; N, 7.87.

3,3'-Diaminodimesityl Ketone.—In 650 cc. of glacial acetic acid 39.8 g. of 3,3'-dinitrodimesityl ketone was suspended, then 130 cc. of water and 35 cc. of concentrated hydrochloric acid were added. It was not found necessary to have the nitro compound completely in solution. With mechanical stirring, zinc dust was added in small portions over a period of four hours, 125 g. in all. The mixture was not allowed to heat appreciably. After all the zinc dust had been added, the stirring was continued for twelve hours. After filtering and washing with acetic acid, the filtrate was cooled with ice and excess of ammonia was slowly added with stirring. The solution should not be allowed to heat during neutralization since this caused contamination with a gummy substance. The amine was dissolved in dilute hydrochloric acid and reprecipitated with excess ammonia; yield 30 g. (91%). It was purified by recrystallization from 50% alcohol, forming yellow needles, m. p. 163–164.5° (corr.).

Anal. Calcd. for $C_{19}H_{24}N_2O$: C, 76.98; H, 8.17; N, 9.46. Found: C, 77.14; H, 8.36; N, 9.40.

3,3'-Diaminodimesitylmethane.—To the zinc amalgam (prepared from 100 g. of zinc) and 30 g. of 3,3'-diaminodimesityl ketone dilute hydrochloric acid (about 1:2) was added and the mixture refluxed approximately twelve hours. From time to time more

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[13] Kohler and Baltzly, THIS JOURNAL, **54**, 4023 (1932).

concentrated acid was added. At the end of this period the yellow diaminodimesityl ketone had entirely dissolved.

The colorless solution was filtered from the remaining amalgam, diluted with ice, and excess ammonia added gradually, avoiding a rise in temperature. The solid was dissolved in hydrochloric acid and reprecipitated; yield, 26 g. (91%). The product was recrystallized from alcohol, m. p. 160–160.5° (corr.).

Anal. Calcd. for $C_{19}H_{26}N_2$: C, 80.79; H, 9.28; N, 9.92. Found: C, 81.10; H, 9.32; N, 11.31.

It will be noted that there is a peculiar discrepancy between the results of the combustions and the nitrogen analyses, although several analyses gave the same results, indicating the compound to be perfectly homogeneous in composition. The hydrochloride of the compound was prepared to be analyzed for chlorine.

Preparation of the Dihydrochloride.—To a suspension of 1 g. of diaminodimesityl methane in about 30 cc. of water, hydrochloric acid was added dropwise. The material first dissolved then a white precipitate formed. On boiling, this dissolved but did not reprecipitate on cooling. The compound was precipitated with concentrated hydrochloric acid, filtered and washed with dilute hydrochloric acid; decomposition about 220–290°. After redissolving and reprecipitating, the melting point was unchanged.

Anal. Calcd. for $C_{19}H_{26}N_2 \cdot 2HCl$: Cl, 19.97. Found: Cl, 19.84.

There would seem to be little question that the compound *is* 3,3′-diaminodimesitylmethane, although no explanation is seen for the anomalous nitrogen analyses.

3,5-Dinitrodimesityl Ketone.—To 10 g. of crude 3,5-dinitro-2,4,6-trimethylbenzoyl chloride[14] and 25 g. of mesitylene, 5 g. of aluminum chloride was added. After mechanical stirring for four days at room temperature, the mixture was heated to 70° for a short time, then decomposed with ice and hydrochloric acid. The solid product was extracted with benzene, the solution filtered from a small amount of sticky solid, and the benzene and excess mesitylene removed with steam. The yellow solid remaining was dissolved in a mixture of 400 cc. of alcohol and 70 cc. of acetone. On cooling, yellow crystals separated. After two further recrystallizations from glacial acetic acid the melting point was constant at 199–200° (corr.).

A mixture of this compound with 3,3′-dinitrodimesityl ketone (prepared by nitration of dimesityl ketone) melted at 149–180°.

Anal. Calcd. for $C_{10}H_{20}N_2O_5$: C, 64.01; H, 5.66; N, 7.86. Found: C, 65.05; H, 5.96; N, 7.74.

Dimesitylmethane.—A mixture of 160 g. of mesitylene and 50 g. of formalin was stirred mechanically and cooled to 0°. Dry hydrogen chloride was passed in rapidly until the solution was saturated. After one and one-half hours powdered zinc chloride was added in small portions, 120 g. in all.

After the reaction had proceeded for about twelve hours, the adhering liquid was filtered off. The solid was boiled with water, cooled, crushed and filtered. It was further treated with concentrated hydrochloric acid, washed, then treated with concentrated ammonia, to remove all excess zinc chloride; yield, 130 g. (77.5%). The compound was purified by vacuum distillation, then crystallization from glacial acetic acid, as colorless crystals, m. p. 133–134° (corr.). Kohler and Baltzly[13] report m. p. 135°.

Attempts to Resolve VII, VIII and IX.—The di-camphor sulfonic acid and dibromocamphor sulfonic acid salts of 3,3′-diaminodimesityl sulfone and 3,3′-diaminodimesityl ketone were prepared in absolute ethyl acetate and sufficient absolute ethyl or methyl alcohol then added to clear the solution. The analogous salts of 3,3′-diamino-

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(14) Kunckell and Hildebrandt, *Ber.*, **34**, 1826 (1901).

dimesitylmethane were made in water. Various fractions obtained by evaporation gave the same rotation and the recrystallized product of each also the same rotation.

TABLE I

ROTATIONS OF SALTS OF VII, VIII AND IX

	3,3′-Diamino-dimesityl	Salt, camphor sulfonic, I; bromocamphor sulfonic, II	0.1000 g. made up to cc.	Solvent, abs.	Temp., °C.	α_D	$[\alpha]_D$
1	Sulfone	I	$10:l = 1$	Alcohol	20	+0.34	+34
2	Sulfone	II	$20:l = 1$	Methanol	27	+ .26	+52
3	Ketone	I	$20:l = 2$	Alcohol	25	+ .28	+25
4	Ketone	II	$20:l = 2$	Methanol	26	+ .58	+58
5	Methane	I	$20:l = 2$	Methanol	28	+ .23	+23
6	Methane	II	$20:l = 1$	Methanol	30[a]	+ .29	+58

	Formula	Analyses, % Calcd.	Analyses, % Found
1	$C_{38}H_{52}N_2O_8S_3$	N, 3.68	3.74
2	$C_{38}H_{50}Br_2N_2O_8S_3$[a,b]	Br, 17.40	16.08
3	$C_{39}H_{52}N_2O_7S_2 \cdot 2H_2O$[c]	C, 61.54; H, 7.43;	61.37; 7.71
		N, 3.68; S, 8.42	3.68; 8.79
4	$C_{39}H_{50}Br_2N_2O_7S_2 \cdot 2H_2O$[c].	C, 50.95; H, 5.92	50.94; 6.12
		N, 3.05; S, 6.98	3.32; 6.75
5	$C_{39}H_{54}N_2O_6S_2$	N, 3.94	4.43
6	$C_{39}H_{52}Br_2N_2S_2O_6$	N, 3.22	3.58

[a] The salt was hygroscopic, which made impossible satisfactory determinations of water of hydration. [b] The analysis indicates a hydrated salt. [c] Solution prepared at 0°.

Summary

The 3,3′-diamino derivatives of dimesitylmethane, dimesityl ketone and dimesityl sulfone have been prepared. Attempts to resolve them resulted in failure.

A discussion is given of the theoretical possibilities in compounds of this type.

URBANA, ILLINOIS
RECEIVED JULY 24, 1933
PUBLISHED NOVEMBER 7, 1933