than the other which projects away from the ring. Furthermore, the ratio of hydrogens to be expected for II is 15 (aromatic):2 (vinyl):11(saturated), which closely approximates the observed 14.4: 1.9:11.8. That the absorption due to the cyclopropyl ring hydrogens falls under that for the methyl group hydrogens undoubtedly is due to the allylic character of the cyclopropyl hydrogens.

This evidence points unequivocally to the structure II for eucarvone enol triphenylmethyl ether. Attempts to isolate any substance corresponding to structure I, either from the crude reaction mixtures, from solutions exposed to sunlight for a period of weeks, or from material heated at 200° have met with failure. Attempts to obtain chemical evidence for structure II by hydrogenation (one mole) followed by hydrolysis to carone or carvenone have failed.

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TRIPLET STATES FROM MAGNETO-OPTICAL ROTATORY DISPERSION STUDIES

Sir:

Optical rotatory dispersion studies have been quite useful for investigating the stereochemistry of compounds[1] and polymers.[2] The technique, however, is limited to naturally optically active molecules. By using a magnetic field[3] in conjunction with the optical rotatory dispersion method, it should be possible to extend the scope of the method to all molecules whether they be optically active or inactive. This type of measurement is called magneto-optical rotatory dispersion and has been the subject of a number of studies.[4]

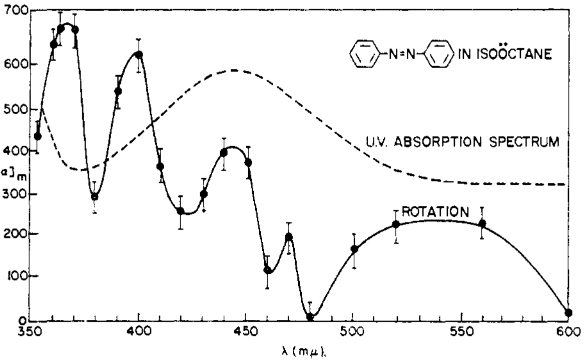

Fig. 1.—A plot of the molar magnetic rotation $[\alpha]_m$ for azobenzene as a function of wave length. The results are calculated from rotations measured in a 1-cm. cell for a 0.1% solution at 30°. $[\alpha]_m = [\theta]_m M/100$ when $[\theta]_m$ and M are the specific magnetic rotation and molecular weight, respectively. The magnitude of experimental error is depicted by the vertical lines at the experimental points.

The initial experiments were conducted on a number of optically inactive compounds and polymers using a Rudolph polarimeter instrument[5] suitably modified to allow the application of the magnetic field of 1200 gauss parallel to the light beam. Figure 1 shows the type of magnetic rotation spectrum obtained for a solution of azobenzene in isoöctane. The results in the region of the long-wave-length absorption band (singlet→singlet transition) of the compound clearly resemble the spectra obtained for optically active compounds by the optical rotatory dispersion technique. Both the magnitude (approximately 700°) and detailed features of the molar magnetic rotation results indicate that such spectra may provide useful stereochemical information about molecules in an analogous manner to the optical rotating dispersion technique. Moreover, the presence of a magnetic rotation peak at 540 mμ outside the region of the singlet →singlet transition shows that factors other than the Cotton effect[6] are involved.

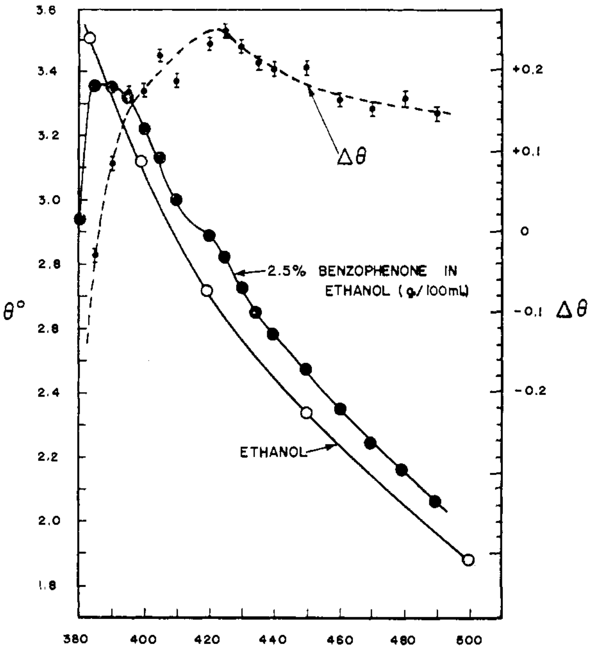

Fig. 2.—A plot of the observed magnetic rotations θ *versus* wave length (λ): the rotations were measured in a 5-cm. cell at 30°: $\Delta\theta = \theta - 0.975\theta_0$ where θ_0 is the rotation for the solvent ethanol.

Figure 2 depicts the observed magnetic rotations (θ) for a solution of benzophenone in ethanol at wave lengths longer than the 265 mμ singlet → singlet absorption band of the compound. A plot of $\Delta\theta$ *vs.* λ gives a magnetic rotation maximum at 425 mμ, quite close to the previously observed singlet → triplet transition for benzophenone at 410 mμ.[7] In phenazine a series of magnetic rotation peaks was obtained at 680, 625, 578, 538, 510 and 490 mμ. These occur at much longer wave lengths

[1] C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., New York, N. Y., 1960.

[2] P. Doty and J. T. Yang, THIS JOURNAL, **78**, 498 (1956).

[3] This in effect is a combination of the Faraday effect with the Cotton effect.[6]

[4] A. Cotton and M. Scherer, *Compt. rend.*, **195**, 1342 (1932); F. H. Garner, C. W. Nutt and A. Labbauf, *J. Inst. Petrol.*, **41**, No. 383, 329 (1955).

[5] Rudolph spectropolarimeter (Model 200AS/80Q/650), Rudolph & Sons, Caldwell, New Jersey. This instrument has a sensitivity of 0.003°. The experimental error in measurement was 0.01°.

[6] A. Cotton, *Compt. Rend.*, **120**, 989 (1895).

[7] G. N. Lewis and M. Kasha, THIS JOURNAL, **66**, 2100 (1944).

than the 365 mμ (singlet → singlet) absorption band for the compound. The maxima correspond quite well with the previously observed vibrational structure of the singlet → triplet transition of phenazine in methyl iodide at 655, 625, 588, 545, and 510 mμ.[8] For polystyrene film a magnetic rotation maximum was observed at 335 mμ, quite close to the triplet-state absorption region for toluene at 347 mμ.[9]

With polymethylmethacrylate, a normal Faraday effect was obtained; however, no magnetic rotation peaks were observed at wave lengths longer than 360 mμ. The above results demonstrate that magnetic rotatory dispersion measurements are useful for detecting the triplet states of certain molecules. A literature search showed that the use of magnetic rotations to detect triplet states is inherent in the theory of the Faraday effect[10] for diatomic molecules. Some experimental evidence for this has been obtained for such molecules as I_2,[11] ICl and IBr.[12] This communication illustrates that the method is also applicable to certain organic compounds and polymers. We are now engaged in examining the scope and utility of magneto-optical rotation spectroscopy.[13]

(8) R. W. Harrell, Ph.D. Thesis, Florida State University, Tallahassee, Florida, January, 1959.

(9) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

(10) R. Serber, *Phys. Rev.*, **41**, 489 (1932).

(11) T. Carroll, *ibid.*, **52**, 822 (1937).

(12) W. H. Eberhardt, Wu-chieh Chung and H. Renner, *J. Mol. Spectroscopy*, **3**, 664 (1959).

(13) The author wishes to thank Drs. H. Kobsa and R. W. Harrell of the Du Pont Company for helpful discussions.

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A NEW TYPE OF ALUMINUM HYDRIDE ADDUCT

Sir:

The Lewis adduct between N,N,N',N'-tetramethylethylenediamine and aluminum hydride, which we have recently prepared, probably constitutes the first example of chelation in compounds of this type. This substance, in addition to being thermally more stable than any previously prepared adduct of aluminum hydride, yields information which may have important consequences affecting the structures of all di-adducts of aluminum hydride.

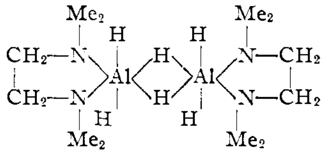
The new compound has been prepared by two procedures, the first of which involved the action of the diamine dihydrochloride on lithium aluminum hydride in an excess of the diamine as a solvent.[1] However, a more convenient route involved treatment of bis-(trimethylamine)-aluminum hydride with an excess of the tertiary diamine at room temperature. In one such preparation,

$$2LiAlH_4 + Me_2NCH_2CH_2NMe_2{\cdot}2HCl \xrightarrow{Me_2NCH_2CH_2NMe_2} 2H_2 + 2LiCl + 2H_3Al{\cdot}Me_2NCH_2CH_2NMe_2$$

$$AlH_3{\cdot}2NMe_3 + Me_2NCH_2CH_2NMe_2 \longrightarrow 2NMe_3 + AlH_3{\cdot}Me_2NCH_2CH_2NMe_2$$

carried out in a tensimeter, 0.473 mmole of $AlH_3{\cdot}2NMe_3$ was found to absorb 0.467 mmole of the diamine and, simultaneously, to release 0.949 mmole of trimethylamine.

The adduct prepared in the above manner was a white solid whose vapor pressures at 99.3° and 119.2° were 1.5 mm. and 10.6 mm., respectively. When a sample prepared using 0.20 mmole of $AlH_3{\cdot}2NMe_3$ as a starting material was completely vaporized at 125°, 0.101 mmole of vapor was found to be present. This indicates that the diamine adduct in question is a dimer. We feel that dimerization occurs through hydrogen bridging, rather than through the difunctional amine, and propose the structure



Each of the aluminum atoms is 6-coördinate, probably with an octahedral configuration.

Infrared spectra of $AlH_3{\cdot}2NMe_3$ and of $(AlH_3)_2{\cdot}(Me_2NCH_2CH_2NMe_2)_2$ both show identical Al–H stretch absorptions at 5.90μ, from which one is tempted to infer that the two substances have closely related structures, and, particularly, that $AlH_3{\cdot}2NMe_3$ is dimeric in the vapor phase. (Determining the molecular size of $AlH_3{\cdot}2NMe_3$ directly by tensimetry is not convenient, owing to the pronounced tendency for this substance to dissociate.) Our proposed structure for this substance makes it unnecessary to invoke a pentacovalency for the aluminum atom.

Unlike other AlH_3 adducts, $(AlH_3)_2{\cdot}(Me_2NCH_2CH_2NMe_2)_2$ showed no tendency to decompose over a 24-hour period at 133°. At the end of this time the ratio of aluminum to hydrogen liberated on hydrolysis was 1.00 to 3.01.

The authors are grateful to the Office of Naval Research for financial assistance in this program.

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(1) This is a modification of the general method developed by Ruff and Hawthorne (THIS JOURNAL, **82**, 2141 (1960)) for the preparation of amine adducts of aluminum hydride.

MAGNETIC OBSERVATIONS OF SOME SUBSTITUTED NICKEL(II) SALICYLALDIMINE COMPLEXES

Sir:

Recently Sacconi, *et al.*,[1,2] have reported magnetic moments (0.5–1.6 B.M.) of N-alkylsalicylaldimine Ni(II) complexes over a temperature range in the fused state and in dibutyl phthalate solution. They interpret their results in terms of a distribution of individual planar molecules over low-lying singlet and triplet states,[3,4] thus accounting for the partial paramagnetism. This anomalous magnetic behavior whereby certain apparently

(1) L. Sacconi, R. Cini, M. Ciampolini and F. Maggio, THIS JOURNAL, **82**, 3487 (1960).

(2) L. Sacconi, R. Cini and F. Maggio, *ibid.*, **79**, 3933 (1957).

(3) C. J. Ballhausen and A. D. Liehr, *ibid.*, **81**, 538 (1959).

(4) G. Maki, *J. Chem. Phys.*, **29**, 1129 (1958).