# Dipole Moments of Methyltropolones and their Bromoderivatives*

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Proceeding with our work on the dipole moments of tropolone and its derivatives,[1] we made experiments on three methyltropolones and seven of their bromoderivatives. They were synthesized by one of us[2] and his collaborators. The position of substituents, which had already been inferred from evidences in organic syntheses,[2] could be confirmed by this physico-chemical method.

**Experimental Results.**—The apparatus and the method of measurement are already given in our previous paper.[1] The results are shown in Tables 1 and 2. The only datum found in literature to be compared with the present results is that of the compound II measured by Tyrell and Mills.[3]

* Read before the scientific meeting of the Chemical Society of Japan held on April 4, 1952.

(1) Y. Kurita, T. Nozoe and M. Kubo, *Bull. Chem. Soc. Japan*, **24**, 10, 99 (1951).

(2) T. Nozoe, T. Mukai, M. Kunori, T. Muroi and K. Matsui, *Sci. Reports Tohoku Univ.*, 1, **35**, 242 (1952).

(3) R. D. Haworth and J. D. Hobson, *J. Chem. Soc.*, **1951**, 561.

Table 1

Dielectric constant and density increments

| | Compounds | $w$ $\times 10^5$ | $\Delta\varepsilon$ $\times 10^4$ | $\Delta d$ $\times 10^5$ |
|---|---|---|---|---|
| I | Methyltropolone | 192 | 192 | 47 |
| | m. p. 50.5—51° | 360 | 346 | 88 |
| | 25° | 542 | 497 | 139 |
| II | Methyltropolone | 336 | 418 | 83 |
| | m. p. 74—76° | 598 | 728 | 141 |
| | 30° | 940 | 1143 | 217 |
| III | Methyltropolone | 150 | 211 | 36 |
| | m. p. 108—110° | 331 | 422 | 75 |
| | 25° | 512 | 663 | 123 |
| IV | Bromomethyltropolone | 321 | 267 | 128 |
| | m. p. 123° | 595 | 445 | 158 |
| | 25.6° | 1086 | 899 | 458 |
| V | Bromomethyltropolone | 227 | 230 | 114 |
| | m. p. 83—85° | 514 | 507 | 215 |
| | 25° | 674 | 677 | 282 |
| VI | Bromomethyltropolone | 230 | 80 | 138 |
| | m. p. 171—172.5° | 334 | 129 | 161 |
| | 25° | 549 | 191 | 209 |
| VII | Dibromomethyltropolone | 271 | 158 | 123 |
| | m. p. 140° | 532 | 324 | 257 |
| | 30° | 834 | 524 | 410 |
| VIII | Tribromomethyltropolone | 265 | 82 | 140 |
| | m. p. 99.5—100.5° | 588 | 176 | 309 |
| | 25° | 766 | 225 | 421 |
| IX | Bromomethyltropolone | 213 | 194 | 94 |
| | m. p. 115° | 412 | 355 | 183 |
| | 30° | 545 | 515 | 216 |
| X | Dibromomethyltropolone | 205 | 139 | 104 |
| | m. p. 140° | 404 | 283 | 202 |
| | 30° | 630 | 404 | 321 |

Table 2

Dipole moments of methyltropolones and their derivatives

| | $t$(°C.) | $\varepsilon_1$ | $d_1$(g./cc.) | $\alpha$ | $\beta$(g./cc.) | $P_{2\infty}$(cc.) | $R_D$(cc.) | $\mu$(D) |
|---|---|---|---|---|---|---|---|---|
| I | 25 | 2.2753 | 0.87129 | 8.69 | 0.263 | 255.5± 1.0 | 37.1 | 3.27±.01 |
| II | 30 | 2.2637 | 0.86637 | 12.02 | 0.222 | 340.9± 1.6 | 37.1 | 3.88±.01 |
| III | 25 | 2.2744 | 0.87132 | 12.48 | 0.240 | 354.0± 8.2 | 37.1 | 3.94±.05 |
| IV | 25.6 | 2.2693 | 0.87036 | 8.38 | 0.455 | 375.9±20.6 | 44.8 | 4.05±.13 |
| V | 25 | 2.2727 | 0.87163 | 9.94 | 0.373 | 445.2± 8.2 | 44.8 | 4.42±.05 |
| VI | 25 | 2.2732 | 0.87221 | 3.39 | 0.224 | 192.0±13.6 | 44.8 | 2.68±.12 |
| VII | 30 | 2.2605 | 0.86614 | 6.51 | 0.510 | 406.6± 3.2 | 52.6 | 4.19±.02 |
| VIII | 25 | 2.2732 | 0.87124 | 2.86 | 0.554 | 247.6± 5.2 | 60.4 | 3.02±.04 |
| IX | 30 | 2.2608 | 0.86648 | 9.54 | 0.372 | 453.8±34.4 | 44.8 | 4.51±.19 |
| X | 30 | 2.2644 | 0.86627 | 6.22 | 0.509 | 389.5±21.2 | 52.6 | 4.27±.13 |

Their value of 3.9 D is in good agreement with ours.

**Discussion.**—The theoretical values for the moments of these compounds with substituents at various presumed positions were calculated as in our previous reports. The bond moment of methyl group substituted in tropolone was assumed to be equal to that in toluene; $\mu(C\text{-}CH_3) = -0.4$ D. The calculated values are compared with the experiment in Table 3. We could thus determine definitely the position of substituents for all the compounds studied, except the compound V, for which we wish to defer our final decision.

Table 3

The position of substituents in methyl tropolones and their derivatives

| Compounds | $\mu_{obs}$(D) | $\mu_{calc}$(D) | The position of substituents |
|---|---|---|---|
| I | 3.27 | 3.41 | 3-Methyltropolone |
| II | 3.88 | 3.76 | 4-Methyltropolone |
| III | 3.94 | 3.90 | 5-Methyltropolone |
| IV | 4.05 | 4.17 | 7-Bromo-3-methyltropolone |
| | | 1.95 | 5-Bromo-3-methyltropolone |
| V | 4.42 | 4.24 | 3-Bromo-4-methyltropolone |
| | | 4.45 | 7-Bromo-4-methyltropolone |
| VI | 2.68 | 2.27 | 5-Bromo-4-methyltropolone |
| | | 2.82 | 3,5-Dibromo-4-methyltropolone |
| | | 3.13 | 5,7-Dibromo-4-methyltropolone |
| VII | 4.19 | 4.42 | 3,7-Dibromo-4-methyltropolone |
| VIII | 3.02 | 2.93 | 3,5,7-Tribromo-4-methyltropolone |
| IX | 4.51 | 4.48 | 3-Bromo-5-methyltropolone |
| X | 4.27 | 4.56 | 3,7-Dibromo-5-methyltropolone |

## Summary

The dipole moments of three methyltropolones and their bromoderivatives were measured in benzene solution at 25° or 30°. The values obtained were compared with the theoretical data for the moments of these compounds with substituents at various presumed positions.

The final decision of the position of substituents were made as shown in Table 3.

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