

SUBSTITUENT EFFECT IN THE TRANSANNULAR π -INTERACTION OF
BICYCLO(3.2.2)NONA-3,6-DIEN-2-ONE DERIVATIVES

Shô Itô, Hitoshi Takeshita, Yoshikazu Shoji, Yasuo Toyooka and Tetsuo Nozoe

Department of Chemistry, Tohoku University

Sendai, Japan

(Received in Japan 7 December 1968; received in UK for publication 20 December 1968)

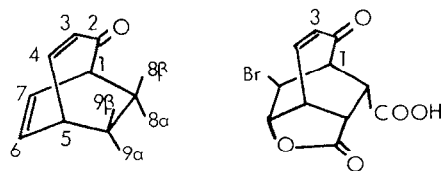
In the course of our study on the Diels-Alder reaction of troponoids using several dienophiles (1,2,3,4,5), we found a novel substituent effect on the transannular π -electron interaction in bicyclo[3.2.2]nona-3,6-dien-2-one system.

Adducts synthesized and their UV maxima are listed in TABLE I.

The parent ring system with an electron attracting substituent at the 8 α - and/or the 9 α -position (compounds I-IV) invariably exhibits, as is expected (6), two maxima (FIGURE), maximum A with higher intensity at ca. 225 m μ (7) and maximum B with lower intensity at around 335 m μ . From their shift in solvents of different polarity, it is clear that the maxima A and B originate from the π - π^* and n- π^* transitions, respectively. Configurational changes at the 8- and 9-positions and/or introduction of various substituents at the 1-position (compounds V-XIII) cause practically no effect on maximum A, although some shifts are observed for maximum B. On the other hand, introduction of halogens (compounds XIV-XXI), methyl group (compounds XXIV, XXV) or methoxyl group (compounds XXII, XXIII) at the 3-position causes the following changes: First, the maximum A shows the bathochromic shift in the increasing order of H through CH₃, Cl and Br, and to OCH₃. However, the magnitude of the bathochromic shift is smaller than that expected from the Woodward rule (6) and the intensity of the maximum decreases in the same order, as shown in TABLE II. Secondly, a third maximum (a shoulder for Cl and CH₃ compounds), designated as maximum A', appears in the range of 260-275 m μ , the wave length and the intensity of the maximum increases in the order CH₃, Cl, Br, OCH₃ (FIGURE). The π - π^*

TABLE I.

Absorption Maxima of Bicyclo[3.2.2]nonen-2-one Derivatives in Methanol.



| Comps. No. | Substituents | | | | | | | $\lambda_{max}^{MeOH} (\mu)(\log \epsilon)$ | | | Ref. | | | |
|---|-------------------|------------------|-----|---|-----|------|-----------|---|------------|------------|-----------|------------|------------|----|
| | Δ^6 series | 3 | 1 | 7 | exo | endo | 8 β | 9 β | 8 α | 9 α | | A | A' | B |
| I | - | - | - | - | - | - | - | - | CN | - | 226(3.89) | - | 338(2.03) | 4 |
| II | - | - | - | - | - | - | - | - | - | CN | 224(3.95) | - | 340(1.95) | 4 |
| III | - | - | - | - | - | - | - | - | CO-O-CO | - | 225(3.80) | - | 337(2.14) | 1 |
| IV | - | - | - | - | - | - | - | - | COOMe | COOMe | 227(3.90) | - | 335(2.30) | 1 |
| V | - | - | OH | - | - | - | - | - | CO-O-CO | - | 225(3.78) | - | 323(2.07) | 3 |
| VI | - | - | OH | - | - | - | - | - | CO-O-CO | - | 225(3.80) | - | 323(2.07) | 3 |
| VII | - | - | OMe | - | - | - | - | - | CO-O-CO | - | 224(3.76) | - | 346(2.06) | 3 |
| VIII | - | - | OMe | - | - | - | - | - | COOMe | COOMe | 226(3.80) | - | 345(1.95) | 3 |
| IX | - | - | Cl | - | - | - | - | - | CN | - | 226(3.81) | - | 332(1.93) | 4 |
| X | - | - | OMe | - | - | - | - | - | CN | - | 225(3.87) | - | 345(2.03) | 4 |
| XI | - | - | OAc | - | - | - | - | - | CN | - | 224(3.86) | - | 332(2.09) | 4 |
| XII | - | - | OAc | - | - | - | - | - | CN | - | 225(3.84) | - | 332(1.79) | 4 |
| XIII | - | - | OAc | - | - | - | - | - | CO-O-CO | - | 224(3.69) | - | 324(2.07) | 3 |
| XIV | Cl | - | - | - | - | - | - | - | CO-O-CO | - | 234(3.81) | 260(3.45)* | 330(2.07) | 2 |
| XV | Cl | - | - | - | - | - | - | - | COOMe | COOMe | 235(3.68) | 260(3.46)* | 333(2.00) | 2 |
| XVI | Cl | - | - | - | - | - | - | - | - | CN | 234(3.72) | 260(3.44)* | 330(1.84) | 4 |
| XVII | Cl | - | - | - | - | - | - | - | CN | - | 237(3.69) | 262(3.47)* | 335(1.90) | 4 |
| XVIII | Cl | - | - | - | - | - | - | - | CN | - | 237(3.66) | 262(3.49) | 332(1.97) | 4 |
| XIX | Br | - | - | - | - | - | - | - | CO-O-CO | - | 245(3.55) | 275(3.47) | 337(2.13) | 2 |
| XX | Br | OMe | - | - | - | - | - | - | CO-O-CO | - | 245(3.50) | 275(3.45) | 340(2.15) | ** |
| XXI | Br | OMe | - | - | - | - | - | - | COOMe | COOMe | 248(3.50) | 275(3.47) | 347(1.80) | ** |
| XXII | OMe | - | - | - | - | - | - | - | CN | - | 231(3.43) | 276(3.48) | **** | 4 |
| XXIII | OMe | - | - | - | - | - | - | - | - | CN | 231(3.51) | 276(3.58) | 325(2.13)* | 4 |
| XXIV | CH ₃ | - | - | - | - | - | - | - | CO-O-CO | - | 235(3.70) | 260(3.2)* | 328(1.99) | ** |
| XXV | CH ₃ | - | - | - | - | - | - | - | COOH | COOH | 236(3.78) | 260(3.3)* | 327(2.24) | ** |
| XXVI | - | OMe | Br | - | - | - | - | - | CO-O-CO | - | 233(3.81) | 270(2.5)* | 345(2.14) | ** |
| <u>Bromo-γ-lactone series ***</u> | | | | | | | | | | | | | | |
| XXVII | - | - | - | - | - | - | - | - | - | - | 232(3.82) | - | 320(1.65) | 1 |
| XXVIII | CH ₃ | - | - | - | - | - | - | - | - | - | 240(3.81) | - | 320(1.81) | ** |
| XXIX | Cl | - | - | - | - | - | - | - | - | - | 250(3.97) | - | **** | 2 |
| XXX | Br | - | - | - | - | - | - | - | - | - | 258(3.84) | - | 320(1.85) | 2 |
| XXXI | Br | OCH ₃ | - | - | - | - | - | - | - | - | 260(3.74) | - | **** | ** |

* Shoulder

** Unpublished compound prepared by Y. T.

*** Positions of bromine and lactone ring might be reversed.

**** Bands are not observed.

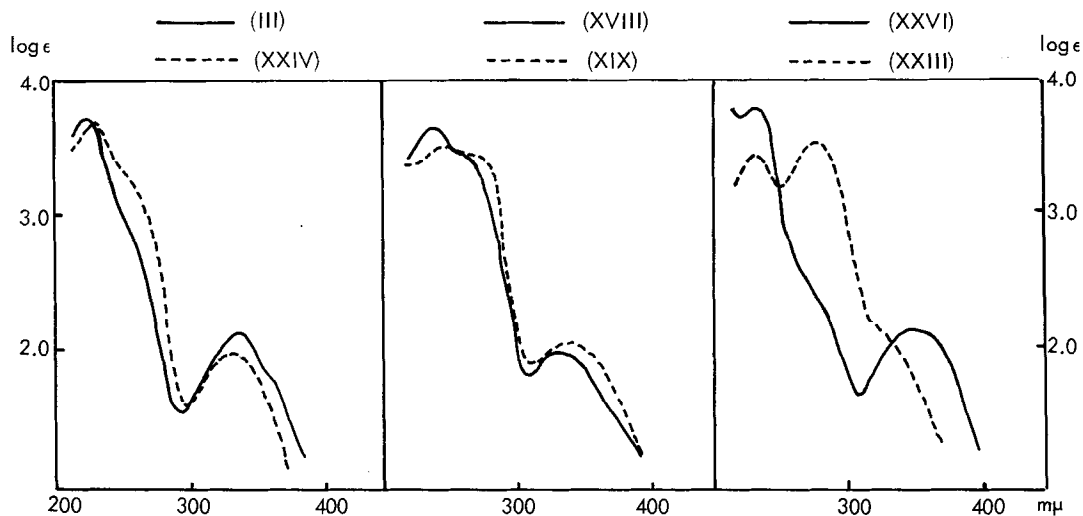


FIGURE
UV Spectra of Bicyclo[3.2.2]nona-3,6-dien-2-one Derivatives.

TABLE II.

Substituent Effect of Absorption Spectra of Bicyclo[3.2.2]nona-3,6-dien-2-one Derivatives.

| Substituent | X=H | X=Cl | X=Br | X=OMe | X=Me | Z=R |
|--|--------------------|-----------|-----------|-----------|-----------|-------|
| $\lambda_{\max A}^{\text{MeOH}} (\text{m}\mu)$ | calcd* 226 | 241 | 251 | 261 | 236 | 226 |
| | obs. 224-227 | 234-237 | 245-248 | 231 | 235-236 | 233 |
| $\log \epsilon_A$ | obs. 3.69-3.95 | 3.66-3.81 | 3.50-3.55 | 3.43-3.51 | 3.70-3.78 | 3.81 |
| $\Delta \lambda_{\max A}^{\text{MeOH}} (\text{m}\mu)$ | obs.-calcd.) -2~+1 | -4~-7 | -3~-6 | -30 | -1~0 | +7 |
| $\lambda_{\max A'}^{\text{MeOH}} (\text{m}\mu)$ | obs. - | 260-262** | 275 | 276 | 260** | 270** |
| $\log \epsilon_{A'}$ | obs. - | ~3.46 | ~3.46 | ~3.53 | 3.25 | 2.50 |
| $\Delta \lambda_{\max (A'-A)}^{\text{MeOH}} (\text{m}\mu)$ | - | 25-26 | 27-30 | 45 | 24 | 37 |
| $\epsilon_{A'}/\epsilon_A$ | - | 0.56 | 0.81 | 1.15 | 0.33 | 0.05 |
| No. of Examples | 11 | 5 | 3 | 2 | 2 | 1 |

* based on the Woodward rule

** shoulder

nature of maximum A' is indicated by measurement in solvents of different polarity. Furthermore, if one compares the frequency separation, $\Delta\lambda_{\max}$, of maxima A and A', with the ratio $\epsilon_{A'}/\epsilon_A$, both are seen to increase in the same order H to OCH₃ as shown in TABLE II. A similar effect is caused by the bromine atom on the isolated double bond (at the 7-position)(XXVI). Since these abnormalities are not observed (TABLE I) for bromolactones (compounds XXVIII-XXXI) without the double bond between C₆ and C₇ (1,2,5), the origin of maximum A' is attributed to a transannular π -interaction in the bicyclo[3.2.2]-nona-3,6-dien-2-one system and the effect of substituent is explicable in terms of the difference in the perturbation caused by the different electron-releasing ability of the substituents, that is, the delocalization of the non-bonded electron pair in halogen or methoxyl oxygen or hyperconjugation of methyl group increases the electron density of $\alpha\beta$ -unsaturated carbonyl system and provides more overlapping with π -electrons in another double bond.

As far as we are aware, no instance of such a substituent dependency in transannular interaction has been noted, and the present result may suggest that the introduction of certain substituents into barrelene (8) and homobarrelenone (9, 10) systems would favor transannular conjugation to give UV spectra considerably different from those of the parent compounds.

Reference and Footnotes

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- 5) Y. Toyooka, Ph.D. Thesis at Tohoku University, 1961.
- 6) A. I. Scott, The Interpretation of UV Spectra of Natural Products, Pergamon Press, Oxford (1964).
- 7) In most cases, maximum A has slight shoulder in its longer wave length side.
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