*Tetrahedron* Vol 32, pp. 2827 to 2830 Pergamon Press 1976 Printed in Great Britain

# CHROMOPHORIC SYSTEMS BASED UPON THROUGH-BOND INTERACTION IV[1-3]

## INTRAMOLECULAR CHARGE-TRANSFER INTERACTION VIA THREE SIGMA BONDS

P. PASMAN, J. W. VERHOEVEN* and TH. J. DEBOER*
Laboratory for Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, Amsterdam, The Netherlands

(*Received UK* 28 *June* 1976; *Accepted for publication* 6 *July* 1976)

**Abstract**—Ketones containing a $\beta$-substituent with readily ionizable lone pair or $\pi$-electrons are studied by UV spectroscopy. When the geometry favours through-bond interaction between the carbonyl group and the $\gamma$-substituent a sigma-coupled transition is observed in the near UV region. Replacement of the CO group by more electronegative systems such as the *gem*-dicyanovinylidene group is shown to enhance the intensity of the sigma-coupled transition and to shift it bathochromically. These phenomena are interpreted to result from a charge-transfer character of the sigma-coupled transition. Furthermore it is shown that intensity borrowing from locally excited states plays an important role in determining the intensity of this sigma-coupled transition.

### INTRODUCTION

The concept of "through-space" and "through-bond" interaction[4-6] has greatly aided the qualitative classification of electronic interactions between functional groups separated by two or more sigma-bonds. A quantitative separation in "through-space" and "through-bond" components has also been attempted but this is much more difficult and often rather arbitrary.[7]

Extensive studies have been directed[8-11] towards the absorption spectra of compounds in which a CO group and a group with lone pair or $\pi$-electrons (e.g. amino, mercapto or vinyl) are separated by two or more sigma-bonds. For such compounds—in addition to change in intensity and absorption maximum of the CO $n \rightarrow \pi^*$ transition[9]—a so called sigma-coupled transition[8] is observed in the 230–260 nm region of the UV spectrum if their conformation fulfills the requirements for efficient through-bond interaction. Thus in the case of three sigma-bonds between $n$ or $\pi$ electron systems an orientation of their orbitals parallel or nearly parallel to the central sigma-bond is required.

For the $\beta$-aminoketone 1-aza-adamantanone **1a** (Table 1), it was recently shown,[1] that the sigma-coupled transition is considerably enhanced and shifted to the red when the carbonyl group is replaced by the more electronegative *gem*-dicyanovinylidene group (**1b**). From the large solvatochromism of the fluorescence for **1b** it was concluded that the sigma-coupled transition has a strong charge-transfer character.

The present paper describes a study on the absorption spectra of compounds containing the *gem*-dicyanovinylidene group or a related electronegatively substituted double bond and a readily ionizable functional group separated by three sigma-bonds.

### RESULTS AND DISCUSSION

The compounds **1-7** compiled in Table 1 all contain the general array A–C–C–D in which D(onor) denotes a group of relatively low ionization potential (D = –NR$_2$, –SR, –OR or –CR=CR$_2$) and A(cceptor) denotes a group with electron acceptor properties. For intramolecular interacting systems—in contrast to the case of intermolecular interactions—dissection into "non-interacting" basis systems is a purely theoretical process and always rather arbitrary on a molecular level. Nevertheless compounds **8** and **9** (Table 1) and **1e – 6e** (Table 2) seem reasonable model systems to estimate the properties of the A resp. D groups in the absence of interaction. In compounds **1–5** the relative orientation of D and A is fixed while in **6** and **7** rotation around the C–D bond is possible.

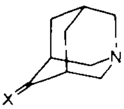
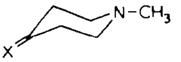
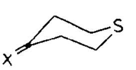
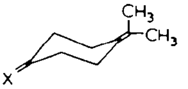
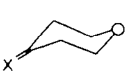
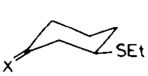
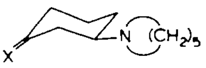
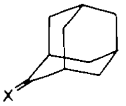
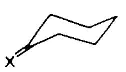
For the bifunctional compounds except **2a, c, 5a** and **7a, c** a sigma-coupled transition is observed (Table 1). Its absence in **2a** has been attributed[8,9] to the axial position of the lone pair on nitrogen which does not fulfill the conformational requirements for through-bond interaction;[5] the same explanation apparently applies to **2c**. From the position of the sigma-coupled transition in the oxa-derivative **5b** (46,700 cm$^{-1}$) and the average blue-shift of 8000 cm$^{-1}$ observed upon going from X = C(CN)$_2$ to X = O a sigma-coupled transition in **5a**, (if any) is calculated to appear at approximately 54,700 cm$^{-1}$ (183 nm). Consequently it is not observed in the near UV region.

The presence of rather strong sigma-coupled transitions for **6b** and **6c** implies that rotamers allowing for through-bond interaction, form a sizable fraction of the total rotameric distribution around the C–D bond in these molecules, but for the nitrogen analogues **7a, c** this is obviously not the case. The present data do not allow any conclusion concerning the eventual influence[12] of the through-bond interaction on this rotameric distribution.

In a localized orbital description the appearance of a sigma-coupled transition in compounds containing the array A–C–C–D can be attributed to the availability of a low lying charge-transfer (CT) configuration A$^-$–C–C–D$^+$ (see Fig. 1). When A is an electronegatively substituted double bond its first $\pi \rightarrow \pi^*$ excited state (energy E$_A$) provides a locally excited configuration A*–C–C–D which is rather close in energy to the CT configuration.

Inspection of the data from Table 1 reveals that the appearance of a sigma-coupled transition is accompanied by weakening of the $\pi \rightarrow \pi^*$ transition for A as compared to its value in the model compounds **8** and **9**. Furthermore

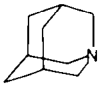
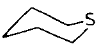
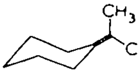
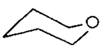
Table 1. Absorption data for sigma-coupled systems (**1–7**) and some reference chromophores (**8–9**). Near UV transitions are given as: $\lambda_{max}$ (nm); [$\tilde{\nu}_{max}$(cm$^{-1}$ × 10$^3$)]; $\epsilon_{max}$(l . mole$^{-1}$ . cm$^{-1}$)

| Structure | No. | X | (C=X) $\pi \rightarrow \pi^*$ | Sigma-coupled | $n \rightarrow \pi^*$ | Solvent | Ref. |
|---|---|---|---|---|---|---|---|
|  | **1a** | O | — | 243[41.1]1366 | 290[34.5]33† | n-hexane | 1 |
| | **1b** | C(CN)$_2$ | 228[43.9]8300 | 317[31.5]4500 | — | n-hexane | 1 |
| | **1c** | C(CN)COOEt | 229[42.7]8780 | 316[31.6]4900 | — | n-hexane | 1 |
| | **1d** | CHCOOEt | 207[48.3]12630 | 275[36.4]4530 | — | n-hexane | 1 |
|  | **2a** | O | — | — | — | cyclohexane | |
| | **2c** | C(CN)COOEt | 240[41.7]14200 | — | — | cyclohexane | |
|  | **3a** | O | — | 233[42.9]640 | 291[34.5]21 | cyclohexane | 15 |
| | **3b** | C(CN)$_2$ | 230[43.5]13500 | 294[34.0]2860 | — | cyclohexane | |
| | **3c** | C(CN)COOEt | 229[43.7]10000 | 288[34.7]2100 | — | cyclohexane | |
| | **3d** | CHCOOMe | 210[47.6]15700 | 254[39.4]2920 | — | cyclohexane | |
|  | **4a** | O | — | ‡ | — | cyclohexane | 16 |
| | **4b** | C(CN)$_2$ | 228[43.9]13000 | 272[36.8]3300 | — | cyclohexane | |
|  | **5a** | O | — | — | 288[34.8]30 | cyclohexane | 17 |
| | **5b** | C(CN)$_2$ | 251[39.8]13000 | 214[46.7]2300 | — | cyclohexane | |
| | **5c** | C(CN)COOEt | 248[40.3]13000 | 210[47.6]5500 | — | cyclohexane | |
|  | **6a** | O | — | 233[42.9]420 | 296[33.8]35 | cyclohexane | 18 |
| | **6b** | C(CN)$_2$ | 238[42.0]12900 | 286[35.0]1680 | — | cyclohexane | |
| | **6c** | C(CN)COOEt | 234[42.7]13800 | 278[36.0]2150 | — | cyclohexane | |
|  | **7a** | O | — | — | — | cyclohexane | 19 |
| | **7c** | CHCOOMe | 213[46.9]15300 | — | — | cyclohexane | |
|  | **8a** | O | — | — | 290[34.5]19 | n-hexane | 1 |
| | **8b** | C(CN)$_2$ | 242[41.3]12000 | — | — | n-hexane | 1 |
| | **8c** | C(CN)COOEt | 242[41.3]14400 | — | — | n-hexane | 1 |
| | **8d** | CHCOOEt | 224[44.6]18150 | — | — | n-hexane | 1 |
|  | **9a** | O | — | — | 280[35.7]26 | cyclohexane | |
| | **9b** | C(CN)$_2$ | 235[42.5]18200 | — | — | cyclohexane | |
| | **9c** | C(CN)COOEt | 235[42.5]14700 | — | — | cyclohexane | |
| | **9d** | CHCOOMe | 218[45.9]15400 | — | — | cyclohexane | |

†Shoulder.

‡Not obtained in pure form (*cf.* experimental).

Table 2. Energies of sigma coupled transitions (h$\nu_\sigma$) in intramolecular donor-acceptor systems and vertical ionization potentials (I$_D$) for model donor compounds as measured by He-I photoelectron spectroscopy

| Compound | h$\nu_\sigma$(eV) | donor model | I$_D$(eV) | Ref. |
|---|---|---|---|---|
| **1b** | 3.90 |  **1e** | 7.94 | 2 |
| **3b** | 4.21 |  **3e** | 8.45 | 19 |
| **4b** | 4.56 |  **4e** | 8.34 | † |
| **6b** | 4.34 | Et$_2$S **6e** | 8.44 | 23 |
| **5b** | 5.79 |  **5e** | 9.50 | 20 |

†This work (see Experimental).

a blue-shift of the $\pi \rightarrow \pi^*$ transition generally occurs when the sigma-coupled transition is located at its long-wavelength side (e.g. **1**, **3**, **4**, **6**), but a red-shift when the sigma-coupled transition lies at its short-wavelength side (e.g. **5**).

These phenomena can be rationalized by assuming interaction between the A$^-$–C–C–D$^+$ and the A*–C–C–D configurations (see Fig. 1) leading to two excited states of "mixed character" with energies $E_1$ and $E_2$ (see Fig. 1).

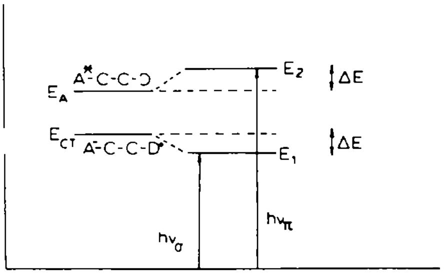


Fig. 1. Interaction diagram for the Charge-Transfer and the first locally (in A) excited configuration.

The sigma-coupled transition ($h\nu_\sigma$) probably borrows[13] most of its intensity from the $\pi \rightarrow \pi^*$ transition through this configuration interaction.†

The interaction diagram of Fig. 1 also rationalizes the general blue-shift observed for the $\pi \rightarrow \pi^*$ transition. From first order perturbation theory this shift can be approximated by $\Delta E = \beta^2/(E_{CT} - E_A)$ where $\beta$ denotes the interaction matrix element between the locally excited and the CT configurations. For **5b** and **5c** $E_A$ and $E_{CT}$ are reversed, leading to a red-shift of the $\pi \rightarrow \pi^*$ transition.

Theoretically[14] $E_{CT}$ can be expressed by:

$$E_{CT} = I_D - E_A - C. \qquad (1)$$

In (1) $I_D$ denotes the ionization potential of a suitable reference donor system (e.g. **1e**–**6e** from Table 2), $E_A$ the electron affinity of A and C measures the Coulomb interaction between $D^+$ and A at a distance $r_{DA}$ ($C \sim e^2/r_{DA}$).

In Table 2 the $h\nu_\sigma$ values for **1b**, **3b**, **4b**, **5b** and **6b** are compared with the $I_D$ values for **1e**, **3e**, **4e**, **5e** and **6e** respectively. A discrete trend towards lower $h\nu_\sigma$ values upon decreasing $I_D$ (i.e. increasing donor capability) is observed which supports the CT character of the sigma-coupled transitions.

The absence of a strict correlation (especially the inversion observed between **3b** and **4b**) has to be attributed to variations of $r_{DA}$ in the series of compounds studied and to the different contributions of locally excited configurations to the CT excited state (see Fig. 1).

In conclusion the present results show that, in systems in which through-bond interaction can occur, substitution of the carbonyl group by a stronger electron acceptor increases the chromophoric effects displayed by these systems, and leads to sigma-coupled transitions which are mainly charge-transfer in nature.

Further research on the theoretical aspects of such chromophoric systems and their applicability in conformational studies is in progress.

## EXPERIMENTAL

All mps are uncorrected. IR spectra were recorded on a Unicam SP 200 spectrometer. UV spectra were recorded on a Cary 14 spectrophotometer. NMR spectra were measured on a Varian A60D instrument.

The photoelectron spectrum of **4e** was measured with a Vacuum Generators ESCA spectrometer, employing He-I emission (21.21 eV) as the ionizing radiation. Calibration was achieved by the use of Ar as an internal reference.

The preparation of **1a–d** and **8a–d** has been described in Ref. 1. Compounds **2c**, **3b–d**, **5b**, **6b**, **7c**, **9b–d** were prepared from the corresponding ketones following the general procedures described in Ref. 1.

N-*Methyl-piperidone*-4 (**2a**) was obtained commercially from "Fluka".

4-*Thia-cyclohexanone* (**3a**) was prepared according to Bennet and Scorak.[15]

4 - *Thia - cyclohexylidene - malonitrile* (**3b**). IR ($CHCl_3$ C=C: 1580; C ≡ N: 2230; NMR ($CDCl_3$): 2.76–3.1 (m); M.p. 111°–114° after recrystallization from methanol.

*Ethyl-4-thia-cyclohexylidene-cyanoacetate* (**3c**). IR ($CHCl_3$) C=C: 1610; C=O: 1730; C ≡ N: 2230; NMR ($CDCl_3$): 4.0–4.5 (2H, q); 2.5–3.5 (8H, m); 1.1–1.6 (3H, t); B.p. 114°/3 mm Hg.

*Methyl-4-thia-cyclohexylidene-acetate* (**3d**). IR ($CHCl_3$) C=C: 1650; C=O: 1700; NMR ($CDCl_3$): 5.6 (1H, s); 3.6 (3H, s); 3.0–3.35 (2H, m); 2.3–3.0 (6H, m); B.p. 60–2°/0.05 mm Hg.

*Isopropylidene cyclohex-4-ylidene-malonitrile* (**4b**). Compound **4a** was prepared by the method of Frank and McPherson.[16] In this reaction a 1 : 1 mixture of **4a** and isopropylcyclohexene-4-one was obtained. This mixture was treated with malonitrile in a Knoevenagel condensation, using piperidine as a catalyst. **4b** was obtained in 20% yield from the reaction mixture by column chromatography with $CHCl_3$ on $SiO_2$. IR ($CHCl_3$) C=C: 1600; C ≡ N: 2250; NMR ($CDCl_3$): 2.70 (4H, m); 2.45 (4H, m); 1.7 (6H, s); M.p. 100°–102° after sublimation (60°/0.05 mm Hg) and recrystallization from MeOH. (Found: C, 77.5; H, 7.5; N, 14.9. Calc. for $C_{12}H_{14}N_2$ (M = 186.25): C, 77.38; H, 7.58, N, 15.04%).

*Isopropylidene cyclohexane* (**4e**) was prepared following the directions of Wallach.[22]

4-*Oxa-cyclohexanone* (**5a**) was prepared according to Owen and Reese.[17]

4-*Oxa-cyclohexylidene-malonitrile* (**5b**). IR ($CHCl_3$) C=C: 1600; C ≡ N: 2230; NMR ($CCl_4$): 3.84 (4H, t); 2.88 (4H, t); M.p. 146°–8° recrystallized from EtOH. (Found: C, 65.0; H, 5.5; N, 18.9. Calc. for $C_8H_8N_2O$ (M = 148.17): C, 64.85; H, 5.44; N, 18.91%).

*Ethyl-4-oxa-cyclohexylidene-cyanoacetate* (**5c**). IR ($CHCl_3$) C=C: 1610; C=O: 1720; C ≡ N: 2240; NMR ($CCl_4$): 4.26 (2H, q); 3.78 (4H, q); 3.14 (2H, t); 2.47 (2H, t); 1.33 (3H, t); M.p. 65°–66° after recrystallization from pentane. (Found: C, 61.7; H, 6.7; N, 7.2. Calc. for $C_{10}H_{13}NO_3$ (M = 195.22: C, 61.52; H, 6.71; N, 7.18%).

3-*Ethylthio-cyclohexanone* (**6a**) was prepared according to Bateman and Shipley.[18]

3-*Ethylthio-cyclohexylidene-malonitrile* (**6b**). IR ($CHCl_3$) C=C: 1600; C ≡ N: 2220.

*Ethyl - 3 - ethylthio - cyclohexylidene - cyanoacetate* (**6c**). IR ($CHCl_3$) C=C: 1610; C=O: 17.30; C ≡ N: 2240; (Found: C, 61.7; H, 7.7; N, 5.6; S, 12.7. Calc. for $C_{13}H_{19}NO_2SCM$ = 253.37): C, 61,62; H, 7.56; N, 5.53; S, 12.66%).

3-*Piperidino-cyclohexanone* (**7a**) was prepared following the procedure of Laryntina.[21]

*Methyl-(3-piperidino)-cyclohexylidene-acetate* (**7c**). IR ($CHCl_3$) C=C: 1650; C=O: 1700; NMR ($CCl_4$): 5.52 (1H, s); 3.55 (3H, s).

*Acknowledgements*—We thank Mr. A. W. J. D. Dekkers for providing preparative data on some of the model compounds, Mr. H. Pieters for carrying out the elemental analyses and Dr. C. Worrell of the University of Utrecht for measurement of the photoelectron spectrum of **4e**. The present investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

## REFERENCES

[1] A. W. J. D. Dekkers, J. W. Verhoeven and W. N. Speckamp, *Tetrahedron* **29**, 1691 (1973).

[2] C. Worrell, J. W. Verhoeven and W. N. Speckamp, *Ibid.* **30**, 3525 (1974).

[3] A. J. de Gee, J. W. Verhoeven, W. J. Sep and Th. J. de Boer, *J. Chem. Soc.* Perkin Trans. II 579 (1975).

[4] R. Hoffmann, A. Imamura and W. J. Hehre, *J. Am. Chem. Soc.* **90**, 1499 (1968).

[5] R. Hoffmann, *Accounts Chem. Res.* **4**, 1 (1971).

[6] R. Gleiter, *Angew. Chem.* **86**, 770 (1974).

[7] E. Heilbronner and A. Schucelzer, *Helv. Chim. Acta* **58**, 936 (1975).

[8] R. C. Cookson, J. Henstock and J. Hudec, *J. Am. Chem. Soc.* **88**, 1060 (1966).

[9] J. Hudec, *Chem. Commun.* 829 (1970).

[10] J. Hudec, *J. Chem. Soc.* Perkin Trans. I 1020 (1975).

[11] C. C. Levin, R. Hoffmann, W. J. Hehre and J. Hudec, *Ibid.* Perkin Trans. I 210 (1973).

[12] R. Gleiter, W. D. Stohrer and R. Hoffmann, *Helv. Chim. Acta* **55**, 893 (1972).

[13] J. N. Murell, *The Theory of the Electronic Spectra of Organic Molecules.* Wiley, New York (1963).

[14] R. Foster, *Organic Charge-Transfer Complexes.* Academic Press, New York (1969).

[15] G. A. Bennet and L. V. A. Scorak, *J. Chem. Soc.* 194 (1927).

---

† For carbonyl compounds the $\pi \rightarrow \pi^*$ transition occurs at much higher energy; intensity borrowing by the sigma-coupled transition from other locally excited configurations (e.g. in *D*) may then become significant.

[16] R. L. Frank and J. B. McPherson, *J. Am. Chem. Soc.* **71**, 1387 (1949).

[17] G. R. Owen and C. B. Reese, *J. Chem. Soc.* (C), 2401 (1970).

[18] L. Bateman and F. W. Shipley, *Ibid.* 1996 (1955).

[19] D. A. Swaigart and D. W. Turner, *J. Am. Chem. Soc.* 5599 (1972).

[20] T. Kohayashi and S. Nagakura, *Bull. Chem. Soc. Japan* **46**, 1558 (1973).

[21] E. A. Laryntina and N. P. Emel'yanow, *Chem. Abstr.* **74**, 760732.

[22] O. Wallach, *Liebigs Ann.* **360**, 26 (1908).

[23] G. Wagner and H. Bock, *Chem. Ber.* **107**, 68 (1974).