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Effect of Halogen and of a Para Substituent on the Solid-State Conformation of Several Crowded Electrophilic Vinyl Halides

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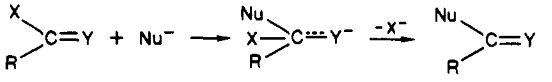
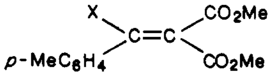
The solid-state conformations of p-$YC_6H_4C(X){=}C(CO_2Me)_2$ [Y = Me, X = Cl (**3**); Y = Me, X = Br (**4**); Y = NO_2, X = Br (**5**)] were determined by X-ray diffraction. Compounds **3** and **4** gave isomorphous crystals with very similar bond lengths (except CX), angles, and torsional angles. It is concluded that the differential steric effects of Cl and Br on the conformations of electrophilic vinyl halides and on the k_{Br}/k_{Cl} ratios in their vinylic substitution are small. The torsional angles of the Ar and the CO_2Me groups in **4** and **5**, which crystallize in different space groups, differ appreciably. This was attributed to crystal packing effects.

The "element effect"[1] is an important mechanistic tool for distinguishing between a single-step and a multistep nucleophilic substitution at an unsaturated carbon. In attack on **1** (X = F, Cl, Br; Y = O, NR′, CR′R″; R′, R″ = electron-withdrawing groups or RC=Y = aryl group), **2** is a transition state in a single-step process and an intermediate in a multistep process (eq 1). In the former case it is predicted that $k_{Br}/k_{Cl} > 1$ and $k_F/k_{Cl} < 1$ since the CX bond is cleaved in the transition state. In the latter case it is usually assumed that the difference in the electron-withdrawing power of the halogens is the main factor that affects the reactivity in the rate-determining nucleophilic attack and hence $k_{Br}/k_{Cl} \sim 1$ and $k_F/k_{Cl} \gg 1$ ratios are predicted. For nucleophilic vinylic substitution in **1** (Y = CR′R″) it was experimentally found that in the vast majority of cases $k_{Br}/k_{Cl} \sim 1$ and $k_F/k_{Cl} \gg 1$.[2-4] Since Cl and Br are assumed to have similar electronic effects, the k_{Br}/k_{Cl} element effect serves as evidence for the multistep nature of the substitution.[2,3] However, this analysis neglects the differences in other properties of the halogens that may affect the relative reactivities of the corresponding vinylic derivatives. Considering only bromine and chlorine, solvation of their anions is different, and this difference was already discussed in criticizing the element effect as a mechanistic probe.[5] The ground-state stabilizating interaction C=C/X is higher by 1.5 kcal mol^{-1} for X = Cl than for X = Br,[6] the hyperconjugative stabilizing CX/Y$^-$ interaction probably differs for X = Cl and Br,[7] and the steric effects of the two halogens may also differ.[8] Consequently, the possibility that the similar reactivities of a vinyl chloride and bromide may sometimes result from compensation of several effects cannot be unequivocally rejected. For example, it may happen that, in a single-step substitution, the better nucleofugality of Br will be compensated by a more hindered approach of the nucleophile to the more hindered vinyl bromide. In a multistep substitution, the higher ground-state C=C/Cl stabilization may be offset by a reduced activation of the system due to the twist of a conjugating α substituent R′ from the double-bond plane, which is less important for X = Cl than for X = Br.


(1)

1 **2**

As part of a program to delineate the importance of the above-mentioned effects, we decided to probe the possible operation of a differential steric effect on the ground state by comparing the solid-state structures of dimethyl β-chloro- and β-bromo-(p-methylbenzylidene)malonates **3** and **4**. The choice of this system was due to several reasons. First, closely related systems were investigated by us in recent years.[9] For example, the k_{Br}/k_{Cl} ratios in substitution of $HCX{=}C(CO_2Me)_2$ by amines in acetonitrile are 0.91–1.07.[9a] Second, a steric effect of the two halogens, if any, should be more pronounced in a congested tetrasubstituted system. Third, the two carbomethoxy groups and the aryl group are conjugated to the double bond, and differential steric effects of Br and Cl should affect the torsional angles of the three groups. The differential stabilization resulting from conjugation could be roughly estimated in this case from the double-bond stabilization parameters of COOMe[10a] and p-MeC_6H_4.[10b] Fourth, the three methyl groups serve as a simple probe to the conformation in solution by their δ values in the ^{1}H NMR spectra.


$$(p\text{-}MeC_6H_4)XC{=}C(CO_2Me)_2$$

3, X = Cl
4, X = Br

Two additional reasons involve comparison with analogues of **3** and **4**. We hoped that change of the p-methyl substituent to an electron-withdrawing one such as p-nitro will give information on a possible contribution of geometrical changes to the Hammett reaction constant.[11] For this reason we also prepared and investigated the p-nitro derivative **5**. In addition, we recently studied the stereochemistry of the substitution of the methyl *tert*-butyl ester **6** (and its (Z) isomer)[12] and of the trideuterated analogue **7**.[13] Differences in the extent of stereoconvergence between systems **6** and **7** may be due to different

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[1] Bunnett, J. F.; Garbisch, E. W., Jr.; Pruitt, K. M. *J. Am. Chem. Soc.* **1957**, *79*, 385.

[2] Rappoport, Z. *Adv. Phys. Org. Chem.* **1969**, *7*, 1.

[3] Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7.

[4] Rappoport, Z.; Rav-Acha, C. *Tetrahedron Lett.* **1984**, *25*, 117.

[5] Bird, R.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1221.

[6] Hine, J. *Structural Effects on Equilibria in Organic Chemistry*; Wiley: New York, 1975; p 273.

[7] Bingham, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 6743.

[8] For a discussion and comparison of the sizes of Cl, Br, and Me groups, see: Hounshell, W. D.; Iroff, L. D.; Iverson, D. J.; Wroczynski, R. J.; Mislow, K. *Isr. J. Chem.* **1980**, *20*, 65.

[9] E.g.: (a) Rappoport, Z.; Topol, A. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1823. (b) *Ibid.* **1975**, 863.

[10] (a) Hine, J.; Kanagabapathy, V. M.; Ng, P. *J. Org. Chem.* **1982**, *47*, 2745. (b) Hine, J.; Skoglund, M. J. *Ibid.* **1982**, *47*, 4766.

[11] It is implicitly assumed in most Hammett type correlations that the conformation of the various substrates is identical. This is not necessarily correct, and when the Ar is bound to an sp^2-hybridized carbon, a change in the conformation of members of the reaction series may contribute either to the value of ρ or to deviations from linearity.

[12] Rappoport, Z.; Gazit, A. *J. Org. Chem.*, following paper in this issue.

[13] Rappoport, Z.; Gazit, A., unpublished results.

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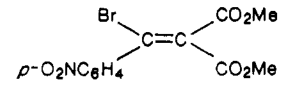

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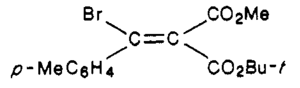

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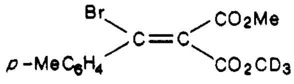

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conformations of the ions **2** derived from **6** and **7**, which in turn may reflect a difference in the ground-state conformations of the neutral diesters. Since the solid-state structure of **6** was reported,[12] comparison with **4** should be interesting.

Results and Discussion

Compounds **3–5** were prepared from the corresponding ethylenes (**8**) via a halogenation (to **9**)–dehydrohalogenation sequence (eq 2). Luckily (see below), the crystals of

$$\mathrm{ArCHO} + \mathrm{CH_2(CO_2Me)_2} \longrightarrow \mathrm{ArCH{=}C(CO_2Me)_2} \xrightarrow{X_2}$$

8a: Ar = p-$\mathrm{MeC_6H_4}$
b: Ar = p-$\mathrm{O_2NC_6H_4}$

$$\mathrm{ArCH(X)C(X)(CO_2Me)_2} \xrightarrow{\mathrm{DBN}} \mathrm{ArC(X){=}C(CO_2Me)_2} \quad (2)$$

9a: Ar = p-$\mathrm{MeC_6H_4}$, X = Cl
b: Ar = p-$\mathrm{MeC_6H_4}$, X = Br
c: Ar = p-$\mathrm{O_2NC_6H_4}$, X = Br

3 and **4** belonged to the same $P\bar{1}$ space group. Unfortunately, **5** crystallized in the $P2_1/c$ space group. The important bond lengths, angles, and dihedral angles are given in Table I. The numbering scheme is given in Figure 1, and since the structures of **3** and **4** resemble one another, only those of **4** and **5** are given. The stereoscopic views are given in the supplementary Figures S1–S3 and other bond lengths and angles and the positional and thermal parameters are given in the supplementary Tables S1–S12.

Crystallographic Data for 3 and 4. Small Differential Steric Effect of Br and Cl on $k_{\mathrm{Br}}/k_{\mathrm{Cl}}$ Ratios. The main conclusion from Table I is that all the crystallographic parameters (obviously excluding the CX bond lengths) are very similar for **3** and **4**. The change from Cl to Br has a negligible effect on the structure within the combined experimental errors. The small differences observed show no discernible trend.

Of special interest to the reactivity in vinylic substitution[2] are the torsional angles of the aryl and the COOMe groups with respect to the double bond. Decrease of the torsional angle of the aryl group should decrease the reactivity due to the stabilizing Ar/C=C interaction. In contrast, lower torsional angles of the COOMe groups are expected to stabilize the double bond by the C=C/COOMe interaction, but to increase the reactivity by increasing the importance of hybrid **10** with a more electrophilic C_β.[14] The torsional angle of the aryl group is reduced from 41° in **3** to 36.5° in **4**. The stabilization energy resulting from a p-tolyl/C=C interaction at full planarity is estimated by Hine as 4.6 kcal mol^{-1}.[10b] As-

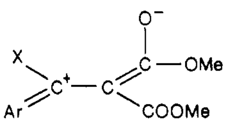

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Table I. Bond Lengths (Å) and Angles (deg) for 3–5

bond	3[a]	4[b]	5[c]	angle	3	4	5	dihedral angle[d]	3	4	5
C(1)–X	1.748 (2)	1.906 (6)	1.900 (5)	X–C(1)–C(7)	113.6 (2)	114.0 (4)	111.6 (4)	A–Ar	131.01	126.46	95.10
C(1)–C(2)	1.339 (3)	1.352 (7)	1.328 (6)	C(7)–C(1)–C(2)	129.2 (2)	129.1 (5)	129.6 (5)	C(7)C(1)X–C(3)C(2)C(5)	5.76	5.15	179.27
C(1)–C(7)	1.479 (3)	1.477 (7)	1.488 (7)	C(3)–C(2)–C(1)	123.3 (2)	121.8 (6)	121.8 (4)				
C(2)–C(3)	1.494 (3)	1.499 (9)	1.476 (7)	C(3)–C(2)–C(5)	116.7 (2)	117.3 (5)	117.0 (5)	A–O(3)C(5)O(4)C(2)	23.25	27.02	90.03
C(2)–C(5)	1.505 (3)	1.494 (7)	1.509 (7)	C(5)–C(2)–C(1)	119.9 (2)	120.8 (5)	121.2 (5)	A–O(1)C(3)O(2)C(2)	92.27	96.29	10.34
C(3)–O(1)	1.191 (2)	1.198 (6)	1.213 (6)	C(2)–C(1)–X	117.2 (2)	116.7 (5)	118.8 (4)	A–C(2)C(3)O(1)	153.46	151.95	169.57
C(3)–O(2)	1.336 (2)	1.332 (6)	1.336 (6)	O(1)–C(3)–O(2)	124.5 (2)	123.8 (5)	124.0 (5)	A–C(2)C(5)O(3)	86.11	83.87	89.75
C(5)–O(3)	1.198 (2)	1.186 (7)	1.201 (7)	O(2)–C(3)–C(2)	109.1 (2)	109.0 (5)	109.9 (4)	O(1)C(3)C(2)–C(2)C(5)O(3)	102.60	105.84	85.38
C(5)–O(4)	1.323 (2)	1.322 (7)	1.329 (6)	O(3)–C(5)–O(4)	124.9 (3)	125.9 (7)	125.5 (5)				
				C(2)–C(5)–O(4)	111.4 (2)	110.8 (5)	111.1 (4)	C(6)O(4)C(5)–O(4)C(5)O(3)	6.22	6.84	0.34
								O(1)C(3)O(2)–C(3)O(2)C(4)	0.76	1.07	0.51
								O(5)NO(6)–Ar			3.40

[a] Aromatic bond lengths: 1.384 (3)–1.391 (3) Å. [b] Aromatic bond lengths: 1.377 (8)–1.401 (9) Å. [c] Aromatic bond lengths: 1.359 (7)–1.386 (6) Å. [d] A = C(7)C(1)XC(3)C(2)C(5) (double-bond plane).

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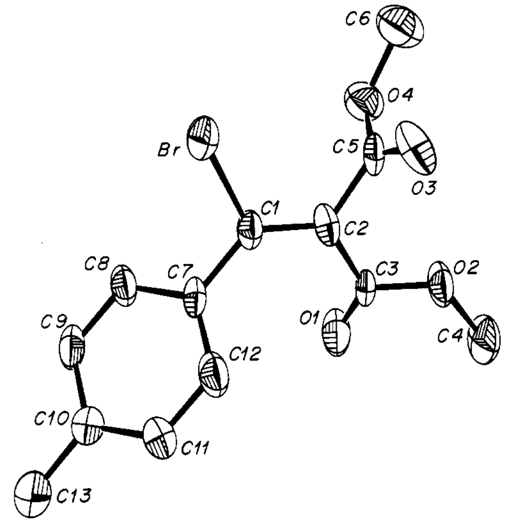
(14) The higher reactivity with thiophenoxide ion of (*E*)-2,4-dinitro-β-bromostyrene compared with that of the (*Z*) isomer was ascribed to a higher planarity (and hence activation) of the (*Z*) isomer: Marchese, G.; Modena, G.; Naso, F. *Tetrahedron* **1968**, *24*, 663.



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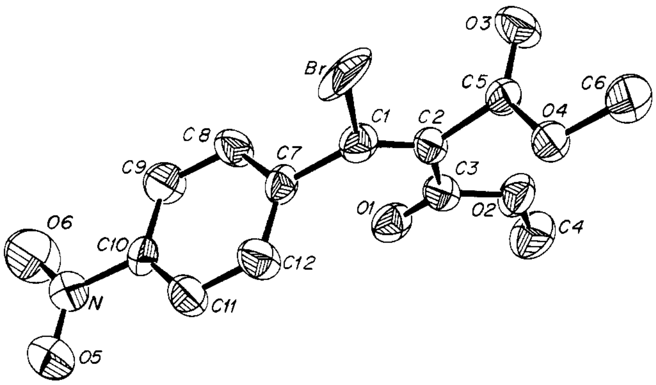

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Figure 1.

suming that the dependence on the torsional angle θ is given by $E = E_0\ [1 + \cos\ (2\theta)]$ where E_0 is the stabilization energy of the planar system,[15] the ground state of **4** is stabilized compared to the ground state of **3** by 0.37 kcal mol^{-1} due to this factor. The torsional angle of the COOMe group cis to the halogen in **3** is lower by 4° than in **4**, and taking a C=C/COOMe stabilization energy of 3.1 kcal mol^{-1},[10a] this difference stabilizes **3** by 0.15 kcal mol^{-1} compared with **4**. The second COOMe group is nearly perpendicular to the double-bond plane in both compounds, and its contribution to the differential stabilization energy is negligible. In conclusion, the combined stabilization energies stabilize **4** more than **3** by 0.2 kcal mol^{-1}. Although the contribution of the small differences in the COOMe torsional angle to the increased charge at C_β of **10** is unknown, it should also be small due to the small difference.[16] If the conclusions based on the solid-state conformation are also applicable to the conformation in solution, the contribution of the ground-state differential steric interaction of bromine and chlorine with the rest of the molecule to the k_{Br}/k_{Cl} should be small.[17] Since we expect that our tetrasubstituted system will be more responsive to steric effects than less substituted systems, the steric effect will contribute even less to the k_{Br}/k_{Cl} ratios in other systems.

Hence, two relevant questions are what is the contribution of crystal packing effects to the similarities and differences in the parameters of **3** and **4** and is there any evidence that their conformations in solution are also similar.

Two parameters in solution that are strongly influenced by the torsional angles are the λ_{max} values in the UV spectra and δ values in the ^{1}H NMR spectra, and both show high similarity for **3** and **4**. In CDCl$_3$, δ(p-Me) for **3** and **4** are identical (2.38) and those for the CO$_2$Me groups cis and trans to the halogen (3.88 and 3.61, respectively, for **3**, 3.86 and 3.57 for **4**) are only 0.02 and 0.04 ppm at a lower field for **3**. Likewise, one pair of the aromatic protons of **3** (δ 7.32, 7.19) is 0.04 ppm downfield, and the other one is only 0.01 ppm downfield compared with those (δ 7.28, 7.18) of **4**. The highest λ_{max} of **3** is at 284 nm (log ϵ 3.90), similar to that for **4** at 286 nm (log ϵ 4.01).

The NMR data suggest that the torsional angles of the aryl groups in **3** and **4** with respect to both the double bond and the ester groups are nearly the same, whereas the UV data indicate that the degree of conjugation of the ester groups with the double bond is nearly identical in both compounds.

Our conclusion is not very surprising in view of the fact that the size of bromine is larger than that of chlorine, but the differences are not very large.[8] The van der Waals radii are 1.95 (Br) and 1.80 (Cl) on Pauling's scale[18] and 2.0 (Br) and 1.73–1.77 (Cl) on Bondi's scale,[19] and the van der Waals volumes are 13.67 (Br) and 11.6–12.2 (Cl) cm^3 mol^{-1}.[19] Rotational barriers around partial and formal double bonds and around sp^2–sp^2, sp^2–sp^3, and sp^3–sp^3 bonds are available for ca. 30 pairs of chlorine and bromine analogues.[20] These mostly reflect increasing crowding in the transition states, but the $\Delta\Delta G^\ddagger = \Delta G^\ddagger$(Br-substituted system) − $\Delta G^\ddagger$(Cl-substituted system) in most cases is <0.5 kcal mol^{-1}, although higher values are known.[21] It seems that the contributions of differential steric effects to the ground-state structure and to the transition state formed in the nucleophilic attack are not large. That the k_{Br}/k_{Cl} ratios are nearly always close to unity for extensively and slightly activated systems and for systems differing extensively in their crowding[2,4] is more consistent with a little contribution of differential steric effect to the k_{Br}/k_{Cl} ratios, than to a large differential effect, which is masked by compensation from other effects.[22]

Comparison with Compound 6. No crystallographic data were reported for compounds ArC(X)=C(CO$_2$R)-CO$_2$R′ according to the Cambridge Crystallographic Data Base.[23] We recently reported such data for compound **6**,[12] which differs from **4** by having a COOBu-t rather than COOMe group cis to the tolyl group. Hence, comparison of the crystallographic data of **4** and **6** is of interest.

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[15] For application of similar equation in probing the energetics of various carbanionic species formed in vinylic substitution, see: Apeloig, Y.; Rappoport, Z. *J. Am. Chem. Soc.* **1969**, *101*, 5095.

[16] In principle, comparison between the reactivities of compounds such as **3** and the planar corresponding Meldrum's acid derivative in vinylic substitution could give information on this point, but data are not available.

[17] From the calculation above the contribution of the ground-state differential steric effect to the k_{Br}/k_{Cl} ratio is lower than a factor of 2.

[18] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University: Ithaca, NY, 1960; p 260.

[19] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

[20] Ōki, M. *Application of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH Publishers: Deerfield Beach, FL, 1985.

[21] Bott, G.; Field, L. D.; Sternhell, S. *J. Am. Chem. Soc.* **1980**, *102*, 5618. Cupas, C. A.; Bollinger, J.-M.; Haslanger, M. *J. Am. Chem. Soc.* **1968**, *90*, 5502. Fuhr, B. J.; Goodwin, B. W.; Hutton, H. M.; Schaefer, T. *Can. J. Chem.* **1970**, *48*, 1558. Carter, R. E.; Marton, J.; Dahlqvist, K.-I. *Acta Chem. Scand.* **1970**, *24*, 195. Nillson, B.; Carter, R. E.; Dahlqvist, K.-I.; Marton, J. *Org. Magn. Reson.* **1972**, *4*, 95. Peeling, L.; Ernst, L.; Schaefer, T. *Can. J. Chem.* **1974**, *52*, 849. Mannschreck, A.; Ernst, L. *Chem. Ber.* **1968**, 5939. *Ibid.* **1971**, *104*, 228. Vögtle, F. *Tetrahedron Lett.* **1969**, 3193.

[22] The few cases where k_{Br}/k_{Cl} ratios are much higher than unity are for the relatively uncrowded β-halostyrenes (cf. ref 3).

[23] We are indebted to Prof. M. Kaftory for this search.

6 crystallizes in the $Pna2_1$ space group, which differs from that of **4**. Surprisingly, most of the nonaromatic bond lengths in **4** are longer (although mostly within the combined experimental errors) than the corresponding ones in the formally bulkier **6**. The two extreme differences are for C(2)–C(3) and C(2)–C(5), which are 1.46 (1) and 1.45 (1) Å in **6**. The differences in most of the bond angles are smaller. The C(3)–C(2)–C(5) angle is 114.5 (9)° in **6** and 117.3 (5)° in **4**. The main difference is that the O(2)–C(3)–C(2) and the C(2)–C(5)–C(4) angles, which are 109.0 and 110.8° in **4**, are widened to 117 and 115° in **6**. The dihedral angles in **6** are much closer to those in **5** than in **4**. The twist angle of the double bond is 3.9°, and the torsional angles of the Ar (20.8°), COOMe (89.3°), and COOBu-*t* (21.5°) in relation to the double bond differ much from those in **4**.

Although these differences could be ascribed to steric and conjugation effects, at present we believe that they are due to different crystal packings. More data are required before distinguishing these alternatives.

Comparison of 4 and 5. We expected that the structure of **4** will resemble that of **5** with modifications resulting from the different electronic properties of Me and NO_2. However, the two structures differ appreciably. Within the experimental errors the C(1)–C(2) and C(2)–C(3) bond lengths are ca. 0.023 Å longer in **4** than in **5**, and the C(1)–C(7), C(2)–C(5), C(3)–O(1), and C(5)–O(3) bonds are longer in **5**. The bond angles are very similar except for Br–C(1)–C(7), which is slightly wider in **4**. The main differences are in the dihedral angles. The twist angles of the double bond are 0.73° in **5** and 5.15° in **4**. The torsional angles ArC=C and C=CCOOMe (cis to Br) of **4** are 54.5 and 27°, whereas in **5** the Ar and COOMe are almost perpendicular to the double-bond plane. The other COOMe group is nearly coplanar (10.3°) with the C=C bond of **5**, but nearly perpendicular to it in **4**.

In both **4** and **5** the C=C and C=O are syn-clinal for the COOMe and syn-periplanar for the second ester group. In all the four ester groups of **4** and **5** the C=O and the OC bonds are nearly eclipsed, in the favourable arrangement for carboxylic esters.[24]

It is difficult to attribute the different torsional angles of **4** and **5** to the electronic effects of the substituents. Since **4** and **5** crystallize in different space groups, we believe that the differences are due to different crystal packing and may not be relevant to the conformation of the molecules in solution.

Conclusions. Our only valid conclusion is that a change of a bromine to chlorine has a small effect on the conformation. Conclusions regarding the effect of the para substituent or the R of COOR on the conformation in solution are unwarranted.

Experimental Section

UV spectra were determined with a Spectronics 2000 spectrophotometer, IR spectra with a Perkin-Elmer 157G spectrometer, ^1H NMR with a Bruker WH-300 pulsed FT spectrometer, and mass spectra on a MAT 311 instrument.

X-ray Crystal Structure Analysis. Data were measured on a PW1100/20 Philips four-circle computer-controlled diffractometer. Mo Kα (λ = 0.71069 Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 22 centered reflections in the range of $11 \leq \theta \leq 15°$ for **3** and **5** and $10 \leq \theta \leq 14°$ for **4**. Intensity data were collected by the ω-2θ technique to a maximum 2θ of 50°. The scan width, $\Delta\omega$, for each reflection was $(1.00 + 0.35 \tan \theta)°$ with a scan speed of 3°/min. Background measurements were made for a total of 20 seconds at both limits of each scan. Three standard reflections were monitored every 60 min. No systematic variations in intensities were found.

Table II. Crystallographic Data

	3	4	5
formula	$C_{13}H_{13}O_4Cl$	$C_{13}H_{13}O_4Br$	$C_{12}H_{10}O_6NBr$
M_r	268.7	313.2	344.1
space gp	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	8.876 (3)	8.985 (2)	7.939 (2)
b, Å	9.589 (3)	9.632 (3)	11.520 (3)
c, Å	8.037 (3)	8.015 (2)	15.667 (3)
α, deg	98.38 (3)	97.30 (3)	
β, deg	88.15 (2)	90.15 (4)	103.22 (5)
γ, deg	104.80 (3)	105.84 (3)	
V, Å^3	654.3 (3)	661.4 (3)	1394.9 (6)
Z	2	2	4
ρ_{calcd}, g cm^{-3}	1.36	1.57	1.64
μ(Mo Kα), cm^{-1}	2.48	30.22	28.81
no. of unique reflcns	2288	1715	2426
no. of reflcns used	1864 [$I \geqslant 3\sigma(I)$]	1535 [$I \geqslant 2\sigma(I)$]	1833 [$I \geqslant 2\sigma(I)$]
R	0.045	0.076	0.055
R_w[a]	0.076	0.093	0.091
x	0.001934	0.019260	0.006050

[a] $w = (\sigma_F{}^2 = xF^2)^{-1}$.

Intensities were corrected for Lorentz and polarization effects. Positions of all non-hydrogen atoms for **3** were taken from the isostructural bromo compound **4**. The Br atom in **4** and **5** was found by Patterson map. After several cycles of refinements[25] the positions of the hydrogen atoms were found and added with a constant isotropic temperature factor of 0.5 Å^2 to the refinement process. Refinement proceeded to convergence by minimizing the function $\sum w(|F_o - F_c|)^2$. A final difference Fourier synthesis map showed several peaks less than 0.25 1 Å^{-3} scattered about the unit cell without a significant feature.

The discrepancy indices, $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, are presented with other pertinent crystallographic data in Table II.

Dimethyl (*p*-Methylbenzylidene)malonate (8a). A mixture of *p*-tolualdehyde (36 g, 150 mmol), dimethyl malonate (42 g, 0.32 mol), piperidine (3 mL), AcOH (2 mL), and dry benzene (150 mL) was refluxed for 24 h in a Dean–Stark apparatus. The mixture was poured into water (300 mL), extracted with CH_2Cl_2 (3 × 100 mL), washed with water, and dried ($MgSO_4$), and the solvent was evaporated, giving an orange oil that solidified on standing. Recrystallization from EtOH gave white leaflets of dimethyl (*p*-methylbenzylidene)malonate: mp 50 °C; 54 g (77%); IR ν_{max} ($CHCl_3$) 3050 (CH), 1730–1680 (CO_2Me), 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.36 (3 H, s, Me), 3.83 (3 H, s, COOMe), 3.85 (3 H, s, COOMe), 7.18, 7.32 (4 H, AB q, centers of 2 d, J = 8 Hz, Ar), 7.74 (1 H, s, =CH); ^1H NMR (C_6D_6) δ 1.96 (3 H, s, Me), 3.38 (3 H, s, COOMe), 3.50 (3 H, s, COOMe), 6.80, 7.23 (4 H, AB q, Ar), 7.85 (1 H, s, =CH). Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 5.98. Found: C, 66.58; H, 5.83.

Dimethyl (*p*-Methylbenzylidene)malonate Dichloride (9a). To a solution of **8a** (11 g, 47 mmol) in CCl_4 (50 mL) was bubbled chlorine gas during 20 min. After standing for 20 h at 20 °C, the mixture was evaporated to dryness and chromatography on silica with CH_2Cl_2–hexane as the eluant gave a colorless viscous oil that solidified on standing to white crystals of dimethyl (*p*-methylbenzylidene)malonate dichloride (**9a**): mp 36–38 °C; 7.6 g (53%); IR ν_{max} (neat) 3000, 2950, (CH), 1750 (CO_2Me) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.34 (3 H, s, Me), 3.68 (3 H, s, MeO), 3.90 (3 H, s, MeO), 5.87 (1 H, s, CHCl), 7.14, 7.42 (4 H, AB q, centers of 2 d, J = 8.2 Hz, Ar); R_f (3:2 CH_2Cl_2–hexane) 0.6 on a silica gel plate. Anal. Calcd for $C_{13}H_{14}Cl_2O_4$: C, 51.16; H, 4.59; Cl, 23.25. Found: C, 51.22; H, 4.65; Cl, 23.69.

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(24) (a) Simonetta, M.; Carrà, S. In *The Chemistry of Carboxylic Acids and Esters*; Patai, S., Ed.; Wiley-Interscience: New York, 1969; Chapter 1. (b) Jones, G. I. L.; Owen, N. L. *J. Mol. Struct.* **1973**, *18*, 1. (c) Ruschin, S.; Bauer, S. H. *J. Phys. Chem.* **1980**, *84*, 3061.

(25) All crystallographic computing was done on a CYBER 855 computer at the Hebrew University of Jerusalem, using the SHELX 1977 Structure Determination Package.

Dimethyl β-Chloro-(*p*-methylbenzylidene)malonate (3). To a solution of **9a** (7 g, 23 mmol) in CH_2Cl_2 (50 mL) was added DBN (3.2 g, 25 mmol) at room temperature. The solution turned red-black. After the mixture was stirred for 18 h, water was added and the organic phase was separated, dried, and evaporated giving an oil that was chromatographed on silica. No olefin **8a** was obtained, but some of unreacted **9a** was recovered. A second chromatography of the product fraction gave a light yellow oil [0.9 g (15%)] that solidified on standing to give **3** as a white solid: mp 40 °C; UV λ_{max} (EtOH) 284 nm (ϵ 7900); IR ν_{max} (neat) 2940 (CH), 1730 (CO_2Me) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.38 (3 H, s, Me), 3.61 (3 H, s, COOMe), 3.88 (3 H, s, COOMe), 7.19, 7.33 (4 H, AB q, $J = 8.2$ Hz, Ar). Anal. Calcd for $C_{13}H_{13}ClO_4$: C, 58.74; H, 4.84; Cl, 13.20. Found: C, 58.37; H, 5.26; Cl, 13.47.

Dimethyl (*p*-Methylbenzylidene)malonate Dibromide (9b). Bromine (8.5 mL, 0.16 mol) was added slowly to a solution of **8a** (33 g, 0.14 mol) in CCl_4 (50 mL). After the mixture was stirred for 4 h at room temperature, water (200 mL) was added and the organic phase was separated, washed with sodium thiosulfate, dried, and evaporated. Crystallization from hexane gave white crystals of dimethyl (*p*-methylbenzylidene)malonate dibromide (**9b**): mp 73 °C; 50 g (90%); IR ν_{max} (neat) 2950 (CH), 1740 (CO_2Me) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.34 (3 H, s, Me), 3.72 (3 H, s, MeO), 3.87 (3 H, s, MeO), 5.68 (1 H, s, CHBr), 7.3 (4 H, AB q, $J = 8$ Hz, Ar); mass spectra, *m/z* (CI) 399, 397, 395, 393 (0.7%, 2%, 2%, 0.7%, M), 355, 353, 351 (4%, 6%, 4%, M − CH_2CO), 315, 313 (100%, M − Br), 287 (5%), 271, 269 (14%), M − Br − CH_2CO), 235 (8%), 233 (4%), 219 (10%), 217 (16%), 201 (10%), 175 (12%), 135 (57%); R_f (60% CH_2Cl_2–40% hexane) 0.6. Anal. Calcd for $C_{13}H_{14}Br_2O_4$: C, 39.61; H, 3.55; Br, 40.58. Found: C, 39.82; H, 3.47; Br, 41.04.

Bromination in AcOH, followed by a similar workup, gave 45% of **9b**.

Dimethyl β-Bromo-(*p*-methylbenzylidene)malonate (4). To a solution of **9b** (8.4 g, 21 mmol) in CH_2Cl_2 (150 mL) was added DBN (3.5 g, 28 mmol). The color was changed first to yellow, then to red, and then to greenish blue. After the mixture was stirred for 32 h at room temperature, water was added and the organic phase was separated, dried, and evaporated. Chromatography on silica (CH_2Cl_2–hexane) gave the olefin **8a** (1.1 g, 23%), traces of **9b**, and dimethyl β-bromo-(*p*-methylbenzylidene)malonate (**4**): mp 42 °C; 1.8 g (28%). Crystals were obtained only after standing for several months: UV λ_{max} (EtOH) 286 nm (ϵ 10 300); IR ν_{max} (neat) 3000, 2950, 2920 (CH), 1730 (CO_2Me) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.38 (3 H, s, Me), 3.57 (3 H, s, COOMe), 3.86 (3 H, s, COOMe), 7.2 (4 H, AB q, $J = 8.5$ Hz, Ar); mass spectra, *m/z* (CI) 314, 312 (5%, 5%, M), 283, 281 (100%, M − MeO), 233 (36%, M − Br), 203 (11%), 174 (6%, M − Br − COOMe), 149 (12%), 119 (5%), 113 (6%). Anal. Calcd for $C_{13}H_{13}BrO_4$: C, 49.85; H, 4.15; Br, 25.53. Found: C, 49.64; H, 4.32; Br, 25.87.

Dimethyl (*p*-Nitrobenzylidene)malonate (8b). A mixture of *p*-nitrobenzaldehyde (15 g, 0.1 mol), dimethyl malonate (18.5 g, 0.14 mol), piperidine (1 mL), and AcOH (1.5 mL) in benzene (100 mL) was refluxed with azeotropic distillation for 66 h. After pouring into water, separation of the layers, extraction with $CHCl_3$, drying, and evaporation of the organic phase, the remainder was crystallized from ethanol, giving 22 g (84%) of pure dimethyl (*p*-nitrobenzylidene)malonate: mp 128 °C; R_f (4:1 CH_2Cl_2–hexane) 0.5; UV λ_{max} (EtOH) 294 nm (29 300); IR ν_{max} ($CHCl_3$) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.85 (3 H, s, COOMe cis to Ar), 3.89 (3 H, s, COOMe trans to Ar), 7.80 (1 H, s, =CH), 7.58, 8.25 (4 H, AB q, $J = 8.6$ Hz, Ar); mass spectra, *m/z* 265 (65%, M), 234 (87%, M − OMe), 205 (95%, M − HCOOMe), 174 (45%, M − HCOOMe − OMe), 166 (100%, $p\text{-}O_2NC_6H_4CH{=}O^+Me$?), 147 (37%, M − 2 COOMe), 101 (29%, M − NO_2 − 2 COOMe). Anal. Calcd for $C_{12}H_{11}NO_2$: C, 54.34; H, 4.15; N, 5.28. Found: C, 54.58; H, 4.30; N, 5.19.

Dimethyl (*p*-Nitrobenzylidene)malonate Dibromide (9c). Bromine (4.6 mL, 86 mmol) was added dropwise at room temperature to a solution of dimethyl (*p*-nitrobenzylidene)malonate (21.5 g, 81 mmol) in $CHCl_3$ (150 mL). After 3 h, the light red solution was poured into water (300 mL) and extracted with $CHCl_3$ (2 × 100 mL) and the combined organic phases were washed with dilute aqueous $Na_2S_2O_3$, dried ($MgSO_4$), and evaporated. An oil (39 g, 86%) that by ^1H NMR contained 90% of the dibromo derivative and 10% of **8b** was obtained.

A small fraction was purified by chromatography on silica, giving a white solid: mp 112 °C; IR ν_{max} ($CHCl_3$) 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.77 (3 H, s, COOMe), 3.92 (3 H, s, COOMe), 5.84 (1 H, s, $CHBr_2$), 7.81, 8.19 (4 H, AB q, $J = 8.8$ Hz, Ar); mass spectra, *m/z* 346, 344 (50%, 51%, M − Br), 318, 316 (8%, 9%, M − Br − CO), 316, 314 (22%, 22%, M − Br − O_2?), 302, 300 (67%, 67%, M − Br − CO_2), 265 (19%, M − 2 Br), 234 (34%, M − MeO − 2 Br), 206 (52%, M − 2 Br − COOMe), 174 (27%, M − 2 Br − HCOOMe − OMe), 166 (100%, $p\text{-}O_2NC_6H_4CH{=}OMe$?), 147 (13%, M − 2 Br − 2 COOMe). Anal. Calcd for $C_{12}H_{11}Br_2NO_6$: C, 33.88; H, 2.59; N, 3.29. Found: C, 34.16; H, 2.80; N, 3.03.

Dimethyl β-Bromo-(*p*-nitrobenzylidene)malonate (5). To a solution of the dibromide **9c** (17 g, 40 mmol) in CH_2Cl_2 (150 mL) was added DBN (8 g, 64 mmol) under argon, and the solution was stirred for 4 h at room temperature. The mixture was poured into water (200 mL), washed with dilute HCl (100 mL), extracted with $CHCl_3$ (2 × 100 mL), and dried ($MgSO_4$), and the organic phase was dried and evaporated. Chromatography of the red oil on silica gel using 20% $CHCl_3$ in hexane as the eluant gave several fractions with different ratios (1.2:19) of **5** to **8b**. Crystallization of the main fraction from ethanol gave 2.45 g (18%) of dimethyl β-bromo-(*p*-nitrobenzylidene)malonate **5**, 97% pure, mp 99 °C. Crystallization of other fractions raised the yield of **5** to 3.95 g (25%): UV λ_{max} (EtOH) 279 nm (12 400); IR ν_{max} 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.63 (3 H, s, COOMe cis to Ar), 3.94 (3 H, s, COOMe trans to Ar), 7.54, 8.27 (4 H, AB q, $J = 8.8$ Hz, Ar); mass spectrum, m/z 345, 343 (22%, 23%, M), 264 (100%, M − Br), 220 (18%, M − Br − CO_2), 205 (11%, M − Br − CO_2Me), 174 (52%, M − Br − COOMe − MeO), 128 (31%, M − Br − COOMe − OMe − NO_2). Anal. Calcd for $C_{12}H_{10}BrNO_6$: C, 41.86; H, 2.90. Found: C, 42.05; H, 3.10.

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Supplementary Material Available: Figures S1–S3 giving stereoscopic views of **3**–**5** and Tables S1–S12 giving bond lengths and angles and positional and thermal parameters (15 pages). Ordering information is given on any current masthead page.