Table II. ^{13}C Chemical Shifts (ppm)[a] of the C-α Carbon in Benzylidene Malononitriles

X	Posner and Hall[7]	Laszlo et al.[33]	this work[b]	Robinson et al.[49]
NMe_2	158.4	158.04	158.01	158.0
OMe	159.1	158.91	158.79	159.0
F		158.44	158.23	158.4
Cl	159.7	158.07		158.2
Br	159.4		158.38	158.4
Me	160.3		159.69	159.8
H	160.8	159.85	159.86	160.1
CN	159.0	156.50	157.31	157.3
NO_2	158.7	157.55	156.77	156.8
solvent	acetone	$CDCl_3$	$CDCl_3$	$CDCl_3$
concn (w/v), %	~5	~25[c]	3	~30

[a] Relative to Me_4Si. [b] Shifts are accurate to ±0.05 ppm and were measured on a FX-200 spectrometer operating at 50.10 MHz. [c] The concentrations used were not specified directly in this study but are assumed to be similar to those of the preliminary study.[8]

similar to that observed in carbonyl systems.[25]

Finally, we note that Laszlo and co-workers do not obtain a good DSP correlation for the C-α position of series 2 (benzylidene malononitriles). In other studies[25] we have measured extensive series of ^{13}C spectra for structurally related compounds and found that when the data are measured with precision, at low concentration, the DSP correlations for the C-α position of a conjugating side chain are of good quality and consistently show a negative polar substituent effect. We note that ^{13}C spectra for substituted benzylidene malononitriles have been measured by three groups (Laszlo et al.,[33] Posner and Hall,[7] and Robinson et al.[49]) and that the SCS values derived differ somewhat. We have therefore carefully remeasured ^{13}C SCS values for a series of these compounds.

An examination of Table II reveals that for the three independent sets of data measured in the same solvent ($CDCl_3$) there is agreement (within experimental error) between our data and that of Robinson et al.[49] However, the data of Laszlo and co-workers[33] for the NO_2 and CN substituents differ from the other two sets by more than the maximum expected experimental error of ±0.2 ppm. Since these are the only two electron-accepting substituents included in the DSP analyses, errors in their SCS values markedly affect the correlations.

DSP analysis of our data gives a good correlation (eq 2)

$$\delta^c = -4.1\sigma_I - 0.7\sigma_R^- \quad SD = 0.19 \quad f = 0.11 \quad (2)$$

provided that the SCS for the NMe_2 substituent is excluded. The observed SCS value for the NMe_2 substituent differs from that predicted from eq 2 by about 8 times the standard deviation, and we have checked that it is not a concentration effect by measuring the shift at a concentration of less than 1% w/v. We suggest that the two highly electron-deficient nitrile groups induce a large through-conjugation effect, hence modifying the electronic properties of this substituent (and hence its SCS value). Similar suggestions have been made by other authors.[22] This conclusion is also implicit in Laszlo's study.[33]

In conclusion, we reemphasize the following points. (1) While in *some* situations there might be no significant improvement in fits obtained by the DSP method compared with single parameter treatments, this is not so in the general case. (2) The ρ_I and ρ_R values obtained from a DSP analysis are extremely useful in assigning mechanistic significance to proposed pathways for the transmission of substituent effects. (3) The SCS data for the two carbonyl groups in **3-5** provide evidence that π-polarization effects may be transmitted (partially) via molecular lines of force.

Acknowledgment. D.C. is the holder of a CSIRO Postdoctoral Studentship, and M.S. is supported by a La Trobe University Postgraduate Award.

Registry No. 2 (X = NMe_2), 2826-28-0; **2** (X = OMe), 2826-26-8; **2** (X = F), 2826-22-4; **2** (X = Br), 2826-24-6; **2** (X = Me), 2826-25-7; **2** (X = H), 2700-22-3; **2** (X = CN), 36937-92-5; **2** (X = NO_2), 2700-23-4.

(49) Robinson, C. N.; Slater, C. D.; Covington, J. S.; Chang, C. R.; Dewey, L. S.; Franceschini, J. M.; Fritzsche, J. L.; Hamilton, J. E.; Irving, C. C.; Morris, J. M.; Norris, D. W.; Rodman, L. E.; Smith, V. I.; Stablein, G. E.; Ward, F. C. *J. Magn. Reson.* **1980**, *41*, 293.

Carbon-13 Nuclear Magnetic Resonance Spectra of 7-Heterotetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptanes. Annelation Effects of Aziridine, Oxirane, and Thiirane Rings. Unusual γ and δ Substituent Effects

Manfred Christl,* Hartmut Leininger, and Erich Brunn

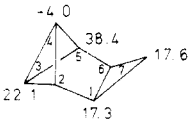
Institut für Organische Chemie, Universität Würzburg, Am Hubland, D 8700 Würzburg, West Germany

Received July 22, 1981

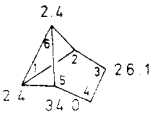
The ^{13}C NMR spectra of 7-heterotetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptanes and of the 7-methyl- and 7-phenyltetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptanes have been measured, and the three-membered-ring annelation effects were determined. The unusual deshielding found for the C-3 resonance in a cyclopropane-annelated cyclopentane derivative (bicyclo[3.1.0]hexane derivative) in the chair conformation carries an even stronger effect in the analogous aziridine-, oxirane-, and thiirane-annelated systems. Substituents in the 7-position of tetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptanes exert unprecedented long-range effects. Literature data of dehydroadamantanes, dehydronoradamantane, [3.3.1]- and [3.1.1]propellanes containing bicyclo[3.1.0]hexane systems are summarized and discussed from the viewpoint of cyclopropane annelation.

In a ^{13}C NMR spectroscopic investigation of the two tricyclo[3.2.1.0^{2,4}]octenes **42** and **44**, Tori et al.[1] discovered two cyclopropane annelation effects, which are observed intramolecularly in tetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptane (**1**) in

0022-3263/82/1947-0661$01.25/0



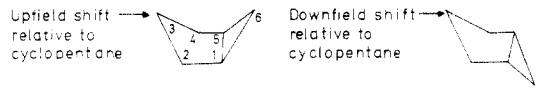
1



2

that the resonances of C-3 and C-4 differ by 26.1 ppm.[2] Compared to the chemical shift of C-1 in tricyclo[3.1.0.0^{2,6}]hexane (**2**), the hydrocarbon devoid of the cyclopropane ring, the C-4 resonance of **1** is shielded by 6.4 ppm, which can be classified as a usual γ effect (γ-syn effect). In contrast, the C-3 signal is deshielded by 19.7 ppm, and this unusual γ-anti effect seems to be caused by the interaction between the unoccupied Walsh orbital of the cyclopropane ring (**36**, X = CH_2) and the highest occupied orbital of proper symmetry (**34**) in the other part of the molecule.

The effects of cyclopropane rings operate, in general, if these are annelated to cyclopentane rings, i.e., if bicyclo[3.1.0]hexane derivatives are considered. In four model compounds (**1**, **3**, **14**, and **44**) containing the boat conformation **3**, the γ-syn effects range from −6.3 to −14.2 ppm

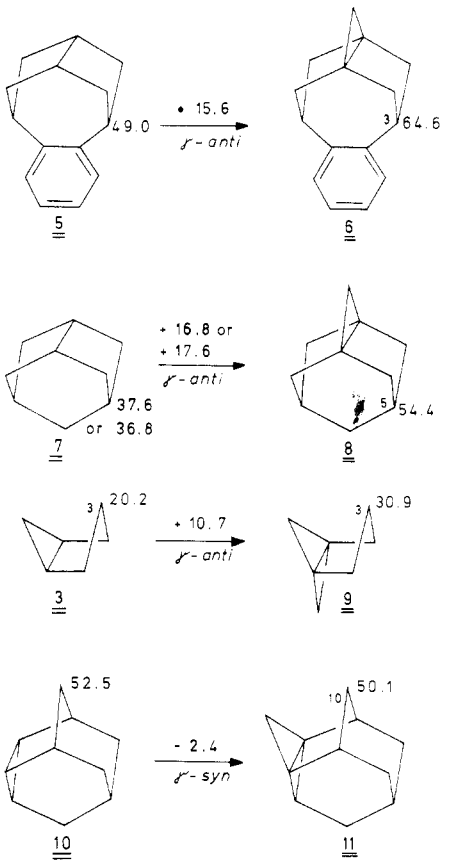


3 4

relative to the corresponding cyclopentanes. If, however, the chair conformation **4** is fixed, three model compounds (**1**, **14**, and **42**) show γ-anti effects of 19.7, 17.1, and 15.2 ppm, respectively.[3]

These effects can be applied to the assignment and the interpretation of the ^{13}C NMR spectra of dehydroadamantanes, dehydronoradamantane, and [3.3.1]- and [3.1.1]propellanes. Scheme I collects four examples from the literature in which, through formal annelation of a cyclopropane ring, a bicyclo[3.1.0]hexane derivative is formed. The surprising low-field absorption of C-3 in **6** requires no special effect of the "inverted carbon atoms" of the propellane bridgeheads,[4] since the γ-anti effect of 15.6 ppm caused at the C-3 resonance by cyclopropane annelation to **5** follows closely the above-mentioned size. Also, in 1,3-dehydroadamantane (**8**)[5] the deshielding of 16.8 or 17.6 ppm observed at the C-5 signal relative to the corresponding absorption of noradamantane (**7**)[6] is expected on the basis of the γ-anti effect. By comparison of [3.1.1]propellane (**9**) with **3**, which prefers the boat conformation, it can be seen that a bicyclo[3.1.0]hexane system in the chair conformation is generated by annelation of the second cyclopropane ring. Only the ^{13}C chemical shifts of **9**, but no assignments, have been reported.[7] Application of the γ-anti effect predicts that the resonance at δ 30.9 belongs to C-3. On formal transformation of 2,4-dehydroadamantane (**10**)[5] to **11**[6] a [3.1.1]propellane system is also formed, but now the new bicyclo[3.1.0]-hexane system is fixed in the boat form. Consequently, an upfield shift has to be expected for the C-10 resonance and is indeed found, although the absolute value of this γ-syn effect is not as great as that of the model compounds.[3]

Scheme I. γ-Syn and γ-Anti Effects on Formal Annelation of a Cyclopropane Ring to a Cyclopentane Derivative[a]



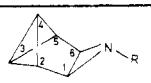
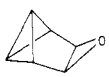
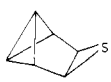
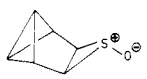
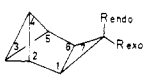
5 6 7 8 3 9 10 11

[a] The numbers on the structures are ^{13}C chemical shifts; the numbers on the arrows are chemical shift differences.

If one starts from a cyclohexane derivative and formally installs a C-1,C-3 bond by removing two hydrogen atoms, these bicyclo[3.1.0]hexane effects can be derived in a second manner, thus allowing an expanded application. Scheme II illustrates the procedure. Compared to the chemical shift of the cyclohexane carbons (**12**), the C-3 resonance of **3** appears upfield by 7.6 ppm, because **3** prefers the boat form. The formal conversion of norpinane (**13**)[8] to **14**[3] produces two bicyclo[3.1.0]hexane systems: one in the boat and the other in the chair conformation. Therefore, the C-7 resonance of **14** is shielded by 8.4 ppm as compared to the chemical shift of the cyclobutane methylene carbons in **13**. On the other hand, C-6, as member of the chair form, shows a deshielding of its resonance by 22.9 ppm. Downfield shifts of similar size are calculated for **6** and 1,3-dehydroadamantane (**8**) relative to **15**[4] and adamantane (**16**), respectively. Although bicyclo[3.1.0]hexane chair derivatives arise in the same way in **10** from **16** and in **17**[3] from **7**, the deshielding effects for the resonances of the carbon atoms in the cyclopentane rings situated opposite to the newly formed bond are considerably decreased. On going from the cyclobutane derivatives **13** and **18**[6] to [3.1.1]propellane (**9**) and its derivative **11**, respectively, one obtains two bicyclo[3.1.0]-hexane systems in each case which share the cyclopentane ring. Accordingly, C-3 in **9** and C-10 in **11** are located syn to one cyclopropane ring and anti to the other. The downfield shifts of their resonances (14.6 and 16.4 ppm) reveal that the chair effect prevails. This is not surprising, as the boat effect, being a usual γ effect, just replaces the

(1) Tori, K.; Ueyama, M.; Tsuji, T.; Matsumura, H.; Tanida, H. *Tetrahedron Lett.* **1974**, 327.
(2) Christl, M. *Chem. Ber.* **1975**, *108*, 2781.
(3) Christl, M.; Herbert, R. *Org. Magn. Reson.* **1979**, *12*, 150.
(4) Duddeck, H.; Klein, H. *Tetrahedron Lett.* **1976**, 1917.
(5) Pincock, R. E.; Fung, F.-N. *Tetrahedron Lett.* **1980**, *21*, 19.
(6) Majerski, Z.; Mlinarić-Majerski, K.; Meić, Z. *Tetrahedron Lett.* **1980**, *21*, 4117.
(7) Gassman, P. G.; Proehl, G. S. *J. Am. Chem. Soc.* **1980**, *102*, 6862.
(8) Weigand, E. F.; Schneider, H.-J. *Org. Magn. Reson.* **1979**, *12*, 637.

Table I. ^{13}C Chemical Shifts (in Parts per Million Downfield from Internal Me_4Si) and One-Bond ^{13}C-H Coupling Constants (in Parentheses) of 7-Hetero-, 7-Methyl-, and 7-Phenyltetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptanes in $CDCl_3$

structure	no.	R	shift, ppm (J, Hz) C-1,6[a]	C-2,5[a]	C-3[a]	C-4[a]	other carbon atoms
	19[b]	H	35.1 (182)	41.2 (169)	27.2 (214)	−5.3 (220)	
	20	$CH_2C_6H_5$	44.6 (178.0)	36.5 (168.4)	21.9 (213.3)	−0.4 (219.9)	CH_2, 59.8 (t, 133.8); C-1′, 139.2 (s); C-2′, C-3′, 127.5, 128.0 (2 d, 159), C-4′, 126.5 (d, 159.6)
	21	C_6H_5	44.9 (182.4)	37.0 (169.9)	24.0 (214.0)	0.4 (220.6)	C-1′, 152.9 (s); C-2′, 120.6 (d, 158.1); C-3′, 128.6 (d, 158.1); C-4′, 121.6 (d, 161.8)
	22	$CO_2C_2H_5$	42.7 (186.1)	38.0 (172.1)	27.3 (214.0)	−0.3 (220.6)	C=O, 161.9 (s); CH_2, 61.6 (t, 147.1); CH_3, 14.4 (q, 126.5)
	23	$CO_2C(CH_3)_3$	42.7 (185.3)	37.9 (172.1)	27.1 (214.0)	−0.1 (220.6)	C=O, 160.8 (s); C, 79.8 (s); CH_3, 27.9 (q, 126.5)
	24	$SO_2C_6H_4$-4-CH_3	46.4 (185.3)	35.9 (173.6)	24.1 (217.7)	0.5 (223.6)	C-1′, 144.0 (s); C-2′, C-3′, 127.7, 129.6 (d, 166.2, 161.8); C-4′, 135.7 (s); CH_3, 21.6 (q, 127.2)
	25		56.9 (189.0)	37.0 (170.6)	26.5 (214.7)	−1.1 (221.8)	
	26		39.1 (181.6)	40.1 (173.1)	31.4 (214.0)	2.0 (219)	
	27		51.7 (183.8)	32.9 (175.0)	8.4 (222.1)	−2.9 (226)	
	28[b]	R_{endo} = H, R_{exo} = CH_3	25.5 (171.0)	37.5 (165.0)	20.0 (208.8)	−3.0 (215)	C-7, 25.2 (d, 161.2); CH_3, 15.9 (q, 125.3)
	29[b]	R_{endo} = CH_3, R_{exo} = H	23.9 (170)	32.2 (165)	22.3 (209.1)	2.6 (215)	C-7, 28.1 (d, 149.5); CH_3, 10.5 (q, 125.6)
	30	R_{endo} = CH_3, R_{exo} = CH_3	32.0 (169)	33.0 (166)	21.6 (211)	3.1 (213)	C-7, 33.2 (s); *endo*-CH_3, 16.9 (q, 126); *exo*-CH_3, 27.9 (q, 125)
	31	R_{endo} = H, R_{exo} = C_6H_5	28.2 (171)	38.2 (167)	21.0 (211)	−2.1 (215)	C-7, 34.9 (d, 162); C-1′, 141.6 (s); C-2′, 125.8 (d, 155.9); C-3′, 127.9 (d, 158.8); C-4′, 125.1 (d, 160.3)
	32	R_{endo} = C_6H_5, R_{exo} = H	24.6 (171)	33.9 (164)	25.2 (207)	2.6 (215)	C-7, 37.9 (d, 164); C-1′, 140.4 (s); C-2′, C-3′, 130.3, 127.6 (2 d, ≃158); C-4′, 125.8 (d, ≃158)
	33	R_{endo} = C_6H_5, R_{exo} = C_6H_5	34.6 (170)	35.1 (166)	25.8 (212)	4.8 (218)	C-7, 51.0 (s); C-1′, 142.4 (s), 146.4 (s); C-2′, C-3′, 131.2, 128.1, 127.9, 127.0 (d, 157–159); C-4′, 125.5, 125.3 (d, 160)

[a] These resonances appear as doublets in the proton-coupled spectra. [b] Solvent C_6D_6.

γ effect exerted by the cyclobutane methylene groups in **13** and **18**.

The examples from Scheme II clearly show that formation of a bicyclo[3.1.0]hexane derivative in the chair conformation from a cyclohexane derivative uniformly results in a substantial deshielding of the C-3 resonance. However, the effect, with actual values of 11.7–25.9 ppm, is subject to wide variation, depending on the individual geometry of the system under consideration and possibly on the strain of the bonds, acting as transmitters.

On replacement of the cyclopropane ring in bicyclo[3.1.0]hexane chair systems with cyclobutane, cyclopentane, or cyclohexane rings, the γ-anti effects rapidly decrease to a small or negligible size.[9] If the five-membered ring of the bicyclo[3.1.0]hexane system is enlarged, the γ-anti effect of the annelated cyclopropane ring also approaches zero.[10]

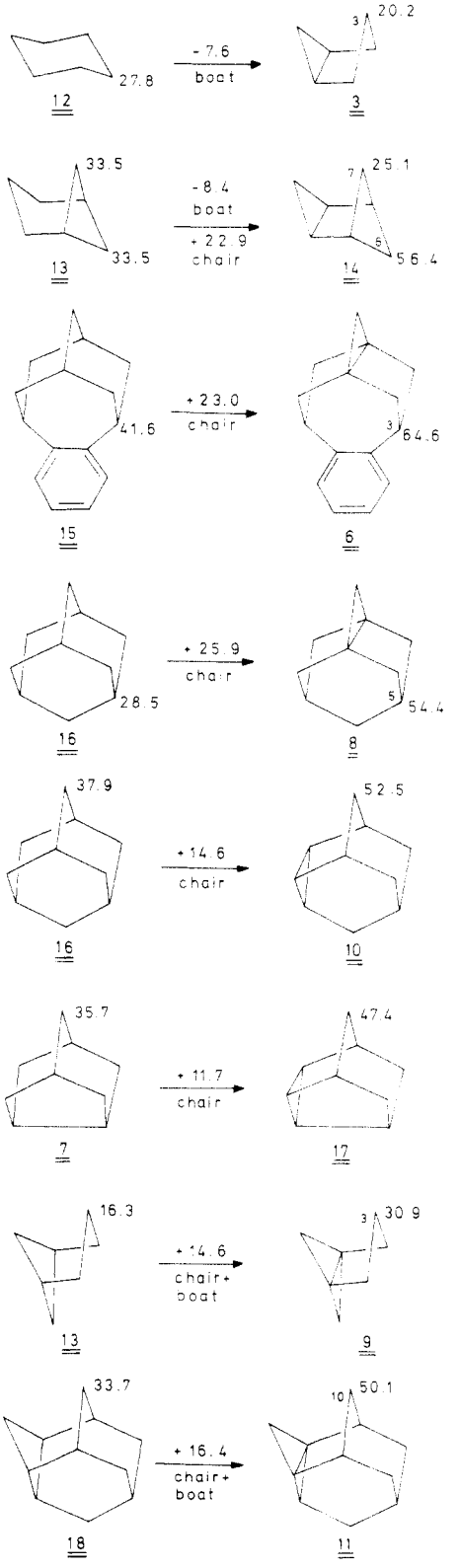
With the annelation effect of the cyclopropane ring in mind, it was intriguing to investigate that of three-membered heterocycles systematically, although some data on oxiranes[11] had already been published. A further target was a study of the influence of substituents at the three-membered rings on the annelation effects.

Results and Discussion

Table I contains the ^{13}C NMR data of the compounds investigated. Complete assignments are possible by means of the proton-coupled spectra on the basis of criteria advanced earlier.[12,13] Thus, the C-3 resonance shows, aside from the characteristically large one-bond ^{13}C–H coupling constant, at most one further doublet of about 4 Hz which is probably caused by H-4. The C-4 signal, however, has more fine structure, frequently consisting of a triplet (about 9 Hz) of doublets (about 4 Hz), indicating coupling to H-1,6 and H-3, respectively. The resonances of C-1,6 and C-2,5 also show multiple fine splittings, which in the

(9) Christl, M.; Herbert, R. *Chem. Ber.* **1979**, *112*, 2022.
(10) Günther, H.; Herrig, W.; Seel, H.; Tobias, S.; de Meijere, A.; Schrader, B. *J. Org. Chem.* **1980**, *45*, 4329.
(11) Davies, S. G.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 2* **1975**, 861.
(12) Christl, M.; Lüddeke, H.-J.; Nagyrevi-Neppel, A.; Freitag, G. *Chem. Ber.* **1977**, *110*, 3745.
(13) Christl, M.; Buchner, W. *Org. Magn. Reson.* **1978**, *11*, 461.

Scheme II. Boat and Chair Effects on Formal Formation of Bicyclo[3.1.0]hexane Derivatives from Cyclohexane Derivatives[a]



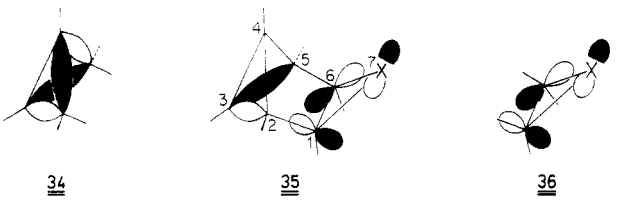
[a] The numbers on the structures are ^{13}C chemical shifts; the numbers on the arrows are chemical shift differences.

former remain below 10 Hz but in the latter always contain a doublet of about 13 Hz. The coupling between C-2 (C-5) and H-5 (H-2) most probably manifests itself in this doublet. Furthermore, in the heterocycles **19–27**, due to the well-known heteroatom effect, the C-1,6 resonance is characterized by a considerably larger one-bond ^{13}C–H coupling constant compared to that of C-2,5. The specific assignments of the chemical shifts in the pairs of endo,exo isomers **28**, **29** and **31**, **32** are achieved by means of the ^1H NMR spectra.

(1) Effect of Annelation of Three-Membered Heterocycles. The annelation effects of three-membered rings are collected in Table II. The size of the α effects, which follows from the chemical shifts of C-1,6, should depend on two major factors: the deshielding owing to the atom added, which increases with increasing electronegativity, and the shielding effect of the three-membered ring formed. For the least electronegative carbon in the cyclopropane derivative **1** a net shielding of 8.8 ppm results, while for the most electronegative oxygen in the oxirane derivative **25** a deshielding of 30.8 ppm is calculated. As expected, the α effects of the aziridine **19** and the thiirane derivative **26** are also deshielding, but less than that of **25**.

The γ-syn effects of the annelated rings move the C-4 resonances upfield. Frequently, these well-known effects reach maximum values if the steric interactions between the groups under consideration are especially severe. From molecular models, the distance between H-4 and H-7_{endo} in **1** is estimated to be about 300 pm. This results in a 6.4-ppm shielding for the C-4 resonance. In the oxirane derivative **25**, the corresponding upfield shift is smaller (3.5 ppm), obviously because the lone pair at the oxygen interacts less seriously with H-4. Since the carbon–sulfur bond in the thiirane derivative **26** is longer than the carbon–oxygen bond in **25**, this tendency continues, and the γ-syn effect nearly vanishes. The aziridine ring in **19**, however, causes the largest shielding (7.7 ppm), possibly indicating the stereochemically unfavorable endo orientation of the nitrogen–hydrogen bond. A smaller γ-syn effect, closer to that of **25**, would be expected if the lone pair at the nitrogen atom occupied the endo position.

The resonances of the carbon atoms in position 3 reveal that the aziridine, oxirane, and thiirane rings cause downfield shifts of 24.8, 24.1, and 29.0 ppm, respectively, thus exhibiting a greater effect than the cyclopropane ring (19.7 ppm). In the case of **1**, this γ-anti effect has been explained on the basis of the interaction between the occupied orbital (see **34**) of the bicyclo[1.1.0]butane system



34 **35** **36**

($1a_2$) and the unoccupied Walsh orbital (see **36**) of the cyclopropane ring ($1a_2'$).[2,3] Formula **35** indicates that for steric reasons overlap occurs only with the lower half of **34**. Therefore, only the C-3 resonance suffers the downfield shift relative to the C-1,6 signal in **2**. At present, it cannot be decided whether this deshielding results from electron back-donation, which necessarily accompanies the orbital interaction described, or from the lower lying excited states within the Karplus–Pople approximation.[14]

The unoccupied Walsh orbitals (**36**) of cyclopropane, aziridine, and oxirane differ significantly.[15] In cyclopropane it is completely symmetric, but in aziridine and oxirane the coefficients of the carbon atoms increase substantially compared to those of the heteroatoms, im-

(14) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; p 102.

(15) (a) Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973. (b) Obtained from MNDO calculations carried out by Professor R. Gleiter, Universität Heidelberg. (c) The MNDO calculation[15b] rules out our earlier assumption[13] concerning the energy of the unoccupied Walsh orbital in halocyclopropanes.

Table II. Three-Membered-Ring Annelation Effects (ppm) in Tetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptane and 7-Heterotetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptanes Calculated by Subtracting the Chemical Shifts of the Appropriate Carbons in Tricyclo[3.1.0.0^{2,6}]hexane (2)

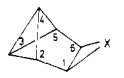
	X	no.	type of three-membered ring	α effect, C-1,6	β effect, C-2,5	γ-anti effect, C-3	γ-syn effect, C-4
	CH_2	1	cyclopropane	−8.8	4.4	19.7	−6.4
	NH	19	aziridine	9.0	7.2	24.8	−7.7
	O	25	oxirane	30.8	3.0	24.1	−3.5
	S	26	thiirane	13.0	6.1	29.0	−0.4

Table III. Effects of 7-Substituents (ppm) in Tetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptanes and 7-Heterotetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptanes Calculated by Subtracting the Chemical Shifts of the Appropriate Carbons in the Corresponding Unsubstituted Compounds

substituent	compds compared	α effect, C-7	β effect, C-1,6	γ effect, C-2,5	δ effect C-3	δ effect C-4
		Tetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptanes				
exo-CH_3	**28-1**	7.6	8.2	−0.9	−2.1	1.0
	30-29	5.1	8.1	0.8	−0.7	0.5
exo-C_6H_5	**31-1**	17.3	10.9	−0.2	−1.1	1.9
	33-32	13.1	10.0	1.2	0.6	2.2
endo-CH_3	**29-1**	10.5	6.6	−6.2	0.2	6.6
	30-28	8.0	6.5	−4.5	1.6	6.1
endo-C_6H_5	**32-1**	20.3	7.3	−4.5	3.1	6.6
	33-31	16.1	6.4	−3.1	4.8	6.9
		7-Azatetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptanes				
$CH_2C_6H_5$	**20-19**		9.5	−4.7	−5.3	4.9
C_6H_5	**21-19**		9.8	−4.2	−3.2	5.7
$CO_2C_2H_5$	**22-19**		7.6	−3.2	0.1	5.0
$CO_2C(CH_3)_3$	**23-19**		7.6	−3.3	−0.1	5.2
$SO_2C_6H_4$-4-CH_3	**24-19**		11.3	−5.3	−3.1	5.8
		7-Thiatetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptane 7-Oxide				
O	**27-26**		12.6	−7.2	−23.0	−4.9

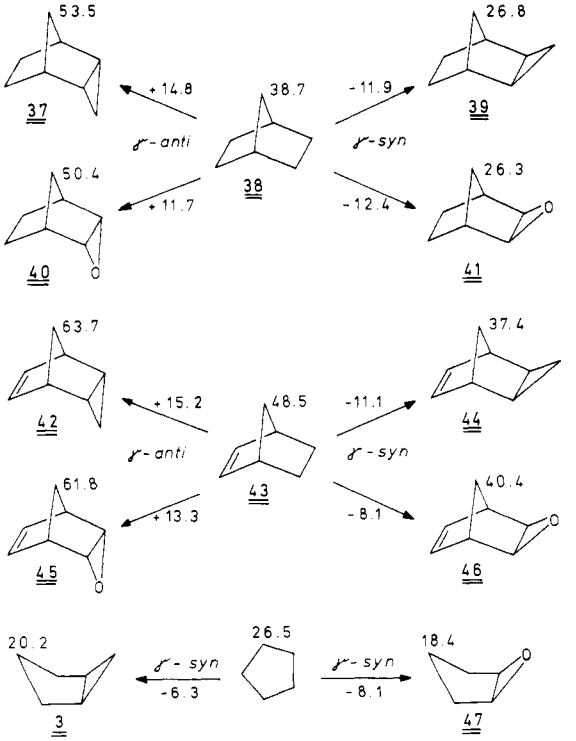
proving the overlap with **34**. The energies of **36** of cyclopropane (X = CH_2, E = 2.79 eV[15b]), aziridine (X = NH, E = 2.87 eV[15b]), and oxirane (X = O, E = 2.63 eV[15b]) are only little different, but that of thiirane (X = S, E = 0.93 eV[15b]) is considerably lower. This also improves the interaction **35** and thus accounts for the extreme γ-anti effect of 29 ppm in **26**.

Scheme III compares published data on relevant oxirane derivatives[11] to those of the corresponding carbocyclic systems. Relative to norbornane (**38**) and norbornene (**43**), the cyclopropane rings in **37**[16] and **42**[1] cause γ-anti effects of 14.8 and 15.2 ppm, respectively, which are larger than those of the oxirane rings in **40** and **45**[11] (11.7 and 13.3 ppm). Therefore, the correlation of the size of the γ-anti effects and orbital properties in **1** and **25** is either accidental or, in the examples of Scheme III, hidden by consequences of different geometry.

The γ-syn effects in Scheme III are larger than those in Table II, as now the three-membered rings face CH_2 groups in the cyclopentane part of the bicyclo[3.1.0]hexane systems, requiring more space than the CH group of position 4 in **1** and **25**. Whereas the oxirane and cyclopropane shieldings in **46**[11] and **44**[1] show the same relative magnitude as in Table II, the values are virtually equal in the pair **41**[11] and **39**.[1] And, in **47**,[11] the oxirane ring is even more effective (−8.1 ppm) than the cyclopropane ring of **3**[2] (−6.3 ppm). Thus, the assumption that the oxirane rings exert smaller γ-syn effects than cyclopropane rings, as in the case of **25** and **1**, is not generally valid.

It can be concluded, however, that oxirane rings within 6-oxabicyclo[3.1.0]hexanes behave in a similar manner as cyclopropane rings within the corresponding carbocyclic systems. The magnitude of the γ-anti and γ-syn effects,

Scheme III. γ-Anti and γ-Syn Effects on Formal Annelation of Cyclopropane and Oxirane Rings to Norbornane, Norbornene, and Cyclopentane



as well as the relative influence of the cyclopropane and oxirane rings, depends considerably on the nature of the ring systems in which the bicyclo[3.1.0]hexane moiety and its 6-oxa derivative are incorporated.

(2) Effects of Substituents in the 7-Position. For the discussion of the influences of the substituents on

(16) Cheng, A. K.; Stothers, J. B. *Org. Magn. Reson.* **1977**, *9*, 355.

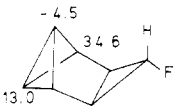
nitrogen in the aziridine derivatives **20–24** relative to **19**, it is useful to know the effects of substituents in the 7-position of **1**. Hence, the upper part of Table III contains the effects of methyl and phenyl groups as calculated from the chemical shifts of **1** and **28–33** (Table I). The α and β effects offer little new information in comparison to the same substituents on cyclohexane. Also, the γ effects which are obtained from the C-2,5 resonances are quite normal. Being cis oriented relative to C-2,5, the endo substituents exert the expected shielding (3.0–6.2 ppm), while exo substituents appear to be of little influence.

Two types of δ effects can be derived: those from the C-3 resonance, which are small, with the exception of those from an endo-phenyl group (deshielding by 3.1 and 4.8 ppm), and those from the C-4 resonance. The latter show a clear-cut distinction between exo substituents, which cause only an insignificant deshielding, and endo substituents, the deshielding of which is unusually large (6.1–6.9 ppm). Most severe steric interactions occur between the CH groups of the 4-position and 7-endo substituents, the δ effects of which almost exactly cancel the γ-syn effect of the cyclopropane ring. Similar influences of several parts per million induced by syn axial δ substituents have been observed occasionally in cyclic molecules.[17,18]

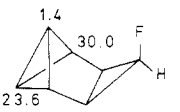
Although extremely different substituents are attached to the nitrogen in the 7-azatetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptanes **20–24**, they cause nearly constant β effects of a size similar to those of the phenyl groups in the carbocycles **31–33**. Without exception, the γ effects are directed to higher field (3.3–5.3 ppm), and the effects induced at the C-4 resonance are directed to lower field (4.9–5.8 ppm) to an even greater extent. In comparison to **28–33**, this would suggest an endo orientation of the N-substituents. This stereochemistry is not supported by the δ effects for the C-3 resonance, however, as they vary from being ineffectual (carboxylate groups) to substantially shielding (benzyl group). This variability possibly mirrors the different interactions of the substituents with the lone pair of the nitrogen atom. An X-ray analysis of **24** has revealed the exo position of the tosyl group in the crystalline state,[19] thus proposing the same invertomer to be favored in solution. Furthermore, the sterically less constrained exo isomers should prevail in **20–23**.

By comparison of the chemical shifts of the episulfoxide **27** with those of the episulfide **26**, the effects induced by the sulfoxide oxygen atom are obtained. Only the β effect is deshielding. The γ and both the δ effects cause upfield shifts, and the size of the δ effect at the C-3 resonance (−23 ppm) is without precedent. According to the literature,[20] on oxidation of thiiranes with peracid, the method we utilize to prepare **27** from **26**,[21] the addition of the oxygen atom always proceeds from the sterically less hindered side, thus suggesting the exo stereochemistry for **27**. This is supported by the ^{1}H NMR resonances which, with the exception of the H-1,6 signal, appear upfield relative to those of **26**.[21] ^{1}H shielding effects of this kind have been used in configurational analysis of episulfoxides.[20] Kellog et al.[22] have reported the ^{13}C NMR data of both the di-*tert*-butylthiiranes and two of the corresponding sulfoxides. There, the oxygens give rise to similar β effects as in **27**; the γ and δ effects, however, are smaller than 2 ppm.

The size of the shielding effects in the bicyclo[1.1.0]-butane system of **27** seems to indicate an electron donation by the oxygen atom. Similar, although smaller, influences are observed upon substitution of the H-7$_{exo}$ of **1** with a fluorine atom as in **48**.[13] Since the unoccupied Walsh orbitals (**36**) of fluorocyclopropane (X = CHF, E = 2.17 eV[15b,c]) and thiirane S-oxide (X = SO, E = −0.12 eV[15b]) have lower energies than those of cyclopropane and thiirane, respectively (vide supra), the interaction **35** should be improved in **27** and **48** relative to that of **26** and **1**,



48



49

respectively. Consequently, the C-3 resonances of **27** and **48** should appear downfield from those of **26** and **1**, respectively. The upfield shifts actually found suggest a counteracting effect, which most probably results from hyperconjugation of a lone pair of oxygen in **27** and of flourine in **48**. Hyperconjugative effects across three bonds have been invoked to explain upfield shifts caused by first-row heteroatoms located at the γ position and antiperiplanar to the ^{13}C nucleus observed.[23] The fact that only 7-F$_{exo}$ as in **48**, where two four-bond zigzags act as transmitters, exerts the upfield shift, but not 7-F$_{endo}$ as in **49**, supports this interpretation.

Even if it is a general feature in ^{13}C NMR spectroscopy that substituent effects are little understood, they undoubtedly hold great value in the analysis of configurations and conformations. The intention of this study is to show on an empirical basis that in polycyclic small-ring compounds substantial γ and δ effects may be operative and that these effects may cause upfield or downfield shifts depending on the stereochemical situation.

Experimental Section

The syntheses of the compounds studied have been described elsewhere: **19**, **21–24**,[24] **20**, **26**,**27**,[21] **25**,[25] **28–33**.[26] ^{13}C NMR spectra were recorded on a Bruker WH-90 spectrometer operating at 22.64 MHz. Proton-coupled spectra were obtained by using the gated decoupling mode. The concentration of the samples was not standardized. The experimental error for the chemical shifts, which were measured relative to Me_4Si, is smaller than 0.1 ppm, and in the coupling constants the last digit of each value given in Table I is uncertain.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous support.

Registry No. **1**, 50861-26-2; **19**, 72393-12-5; **20**, 80063-05-4; **21**, 72393-08-9; **22**, 72393-09-0; **23**, 72393-10-3; **24**, 72393-11-4; **25**, 73688-12-7; **26**, 80063-06-5; **27**, 80063-07-6; **28**, 77429-85-7; **29**, 77481-22-2; **30**, 77429-86-8; **31**, 77429-87-9; **32**, 77481-23-3; **33**, 77429-88-0.

(17) Grover, S. H.; Guthrie, J. P.; Stothers, J. B.; Tan. C. T. *J. Magn. Reson.* **1973**, *10*, 227. Grover, S. H.; Stothers, J. B. *Can. J. Chem.* **1974**, *52*, 870.

(18) Engelhardt, G.; Jancke, H.; Zeigan, D. *Org. Magn. Reson.* **1976**, *8*, 655.

(19) Carried out by Dr. C. Burschka, Institut für Anorganische Chemie der Universität Würzburg.

(20) Kondo, K.; Negishi, A. *Tetrahedron* **1971**, *27*, 4821.

(21) Leininger, H. Dissertation Thesis, Universität Würzburg, 1981.

(22) Raynolds, P.; Zonnebelt, S.; Bakker, S.; Kellog, R. M. *J. Am. Chem. Soc.* **1974**, *96*, 3146.

(23) Eliel, E. L.; Bailey, W. R.; Kopp, L. D.; Willer, R. L.; Grant, D. M.; Bertrand, R.; Christensen, K. A.; Dalling, D. K.; Duch, M. W.; Wenkert, E.; Schell, F. M.; Cochran, D. W. *J. Am. Chem. Soc.* **1975**, *97*, 322.

(24) Christl, M.; Leininger, H. *Tetrahedron Lett.* **1979**, 1553.

(25) Leininger, H.; Christl, M. *Angew. Chem.* **1980**, *92*, 466; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 458.

(26) Christl, M.; Brunn, E. *Angew. Chem.* **1981**, *93*, 474; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 468.