Lumiflavin, the photoproduct of riboflavin, is more stable to light than riboflavin. Accordingly, lumiflavin SERRS spectra show less variability over the time normally required to obtain a Raman spectrum.

Conclusions

We conclude that the previously reported SERRS of flavoproteins do not represent the proteins themselves, but rather their dissociated flavins. Our study includes a selection of flavorpoteins sufficiently varied to suggest that great caution will be necessary in the interpretation of the SERRS spectrum of any flavoprotein. A recent report[1a] of extraction of porphyrins from several heme proteins on colloidal silver suggests that SERS study of protein/small molecule complexes may be generally perilous.

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Determination of the Absolute Configuration of Six-Membered-Ring Ketones by ^{13}C NMR

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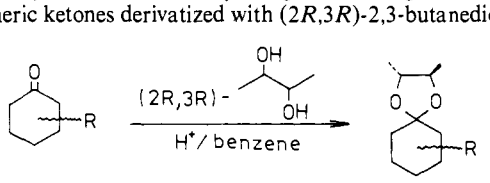
Abstract: The diastereotopic splitting of the ^{13}C NMR signals of the (2*R*,3*R*)-2,3-butanediol acetals of 39 chiral six-membered-ring ketones, including 2- and 3-substituted cyclohexanones, 2-alkyltetrahydropyran-4-ones, and 2- and 3-alkyltetrahydrothiopyran-4-ones, has been studied. The stereodifferentiation of the six-membered-ring carbon atoms was shown to follow a very regular pattern, which is independent of substituents or of heteroatoms in the ring. Hence, an empirical rule could be deduced which allows the assignment of the absolute configuration of the original ketones from the ^{13}C NMR spectrum of their acetals. The rule is only valid for six-membered-ring ketones having the chair form as the preferred conformation in the acetal. As shown for 11 examples, this rule is not valid for acyclic ketones, cyclopentanones, cycloheptanones, or cyclohexanones and cyclohexenones not having the chair form as the preferred conformation. The rule also permits the interpretation of the ^{13}C NMR spectrum of the (2*R*,3*R*)-2,3-butanediol acetals of achiral cyclohexanones (seven examples). The stereodifferentiation is almost exclusively determined by the centers of chirality in the dioxolane ring.

Convenient routes to optically active six-membered-ring ketones have been developed by several research groups. Enantiomerically enriched 2- and 3-substituted cyclohexanones have been obtained from enantioselective reductions of racemic cyclohexanones with HLAD (horse liver alcohol dehyrogenase).[1-5] Cyclohexanones substituted at position 2 have also been synthesized by asymmetric alkylation of cyclohexanone.[6] Optically active 3-(arylthio)- and 3-(arylseleno)cyclohexanones have been obtained from asymmetric conjugate additions of arylthiols and arylselenols to 2-cyclohexenones.[7,8] Optically active 2-alkyltetrahydropyran-4-ones and 2- and 3-alkyltetrahydrothiopyran-4-ones have been obtained from HLAD-catalyzed reduction and oxidation reactions.[9-11] In all these projects the determination of the enantiomeric excess and of the absolute configuration of these ketones is a major element of concern.

The enantiomeric excess has been determined by the method developed by Hiemstra and Wynberg[12] according to which the enantiomeric ketones derivatized with (2*R*,3*R*)-2,3-butanediol into



the corresponding diastereoisomeric acetals. The enantiomeric excess in the original ketones is then obtained by integrating the ^{13}C NMR signals of two diastereotopic carbon atoms of the acetals.

The absolute configuration has been determined by various methods such as octant rule analysis of the Cotton effects and chemical correlation with products of known configuration. It has now been found that the absolute configuration of six-membered-ring ketones can be determined directly from the ^{13}C NMR spectra of the acetals used in the method of Hiemstra and Wynberg.[12] An empirical rule will be formulated.

Discussion

1. Chiral Six-Membered-Ring Ketones. In Tables I and II the ^{13}C chemical shift values (δ) are collected for the six-mem-

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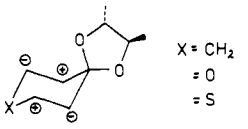

Figure 1. The model.

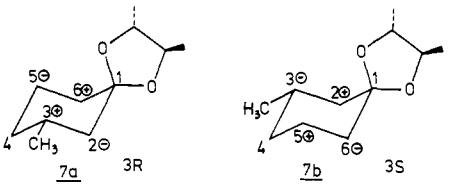

Figure 2. Both enantiomers of **7** acetalyzed with (2*R*,3*R*)-2,3-butanediol and fitted in the model (Figure 1).

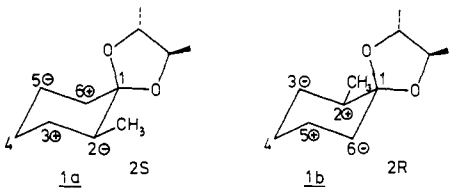

Figure 3. Both enantiomers of **1** acetalyzed with (2*R*,3*R*)-2,3-butanediol and fitted in the model (Figure 1).

bered-ring carbon atoms of the (2*R*,3*R*)-2,3-butanediol acetals of some cyclohexanones, tetrahydropyran-4-ones, and tetrahydrothiopyran-4-ones, respectively. In these tables the diastereoisomeric acetals are differentiated as **a** and **b**, the **a** acetals having the lower δ values in columns II and V and the higher δ values in columns III and VI.

As can be seen in Tables I and II, the **a**, **b** notation is not systematically related to the *R*,*S* assignment. Obviously, the correlation between the chemical shifts and the *R*,*S* assignments shows many inversions. However, these inversions have no stereochemical origin but are a consequence of the use of the nomenclatural numbering rules[15] and of the Cahn–Ingold–Prelog sequence and chirality rules.[16,17] When all acetals, collected in Tables I and II, are fitted in the model shown in Figure 1, a very consistent relationship between the δ values and the absolute configuration of the original ketones can be found. It can be expressed by the following rule: "For each pair of diastereotopic ring carbon atoms,[18] the carbon atom coinciding with a + position in the model has a higher chemical shift than the one coinciding with a − position." A few examples will be discussed in more detail now.

1.1. Cyclohexanones Substituted at Position 3. In Figure 2 the acetals of both enantiomers of 3-methylcyclohexanone **7** are represented after superposition with the model (Figure 1). This shows that C-2 of the 3*S* enantiomer, which has the higher ^{13}C chemical shift (see Table I), occupies a + position, whereas C-2 of the 3*R* enantiomer, which has the lower ^{13}C chemical shift (see Table I), occupies a − position. On the other hand, C-6 of the 3*S* enantiomer has the lower ^{13}C shift and occupies a − position, whereas C-6 of the 3*R* enantiomer has the higher shift and occupies a + position. In the same way, C-3 of the 3*S* enantiomer, occupying a − position, is found to have a lower ^{13}C NMR shift than C-3 of the 3*R* enantiomer which occupies a + position, and C-5 of the 3*S* enantiomer, occuping a + position, has a higher ^{13}C NMR shift than C-5 of the 3*R* enantiomer which occupies a − position. Completely analogous results are found for all

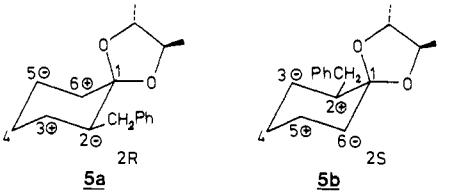

Figure 4. Both enantiomers of **5** acetalyzed with (2*R*,3*R*)-2,3-butanediol and fitted in the model (Figure 1).

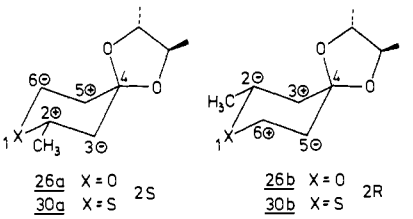

Figure 5. Both enantiomers of **26** and **30** acetalyzed with (2*R*,3*R*)-2,3-butanediol and fitted in the model (Figure 1).

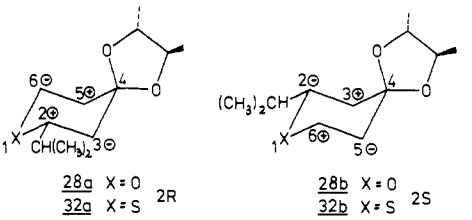

Figure 6. Both enantiomers of **28** and **32** acetalyzed with (2*R*,3*R*)-2,3-butanediol and fitted in the model (Figure 1).

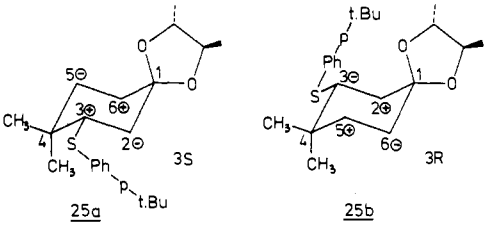

Figure 7. Both enantiomers of **25** acetalyzed with (2*R*,3*R*)-2,3-butanediol and fitted in the model (Figure 1).

3-substituted cyclohexanones (**7**–**24**).

1.2. Cyclohexanones Substituted at Position 2. By comparing the configurations and the ^{13}C chemical shifts of 2-methyl- (**1**) and 3-methylcyclohexanone (**7**) in Table I, one observes an apparent inversion of the correlation between the absolute configuration and the chemical shifts. However, after both diastereoisomeric acetals of 2-methylcyclohexanone are fitted into the model (Figure 3), it becomes clear that all carbon atoms with higher chemical shift values, i.e., C-3 and C-6 of the 2*S* enantiomer and C-2 and C-5 of the 2*R* enantiomer, occupy a + position and all carbon atoms with lower shift values, i.e., C-2 and C-5 of the 2*S* enantiomer and C-3 and C-6 of the 2*R* enantiomer, occupy a − position.

2-Ethyl- (**2**), 2-propyl- (**3**), and 2-decylcyclohexanone (**4**) are completely analogous to 2-methylcyclohexanone (**1**). For 2-benzyl- (**5**) and 2-(methoxymethyl)cyclohexanone (**6**) again an inversion of *R*/*S* labels is observed. This inversion, however, is only the result of the priority assignment by the Cahn–Ingold–Prelog sequence rules, but as can be seen in Figure 4, our rule still holds.

1.3. Substituted Tetrahydropyran-4-ones and Tetrahydrothiopyran-4-ones. The examples given in Figures 5 and 6 show that the rule also holds for substituted tetrahydropyran-4-ones and tetrahydrothiopyran-4-ones (see Table II) and that it is independent from the ring numbering and from the Cahn–Ingold–Prelog sequence rule (compare Figures 5 and 6).

1.4. Polysubstituted Cyclohexanones. Finally the rule also seems to hold for polysubstituted cyclohexanones. An example is given in Figure 7.

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(20) Bordeaux, D.; Gagnaire, G. *Tetrahedron Lett.* **1982**, *23*, 3353.

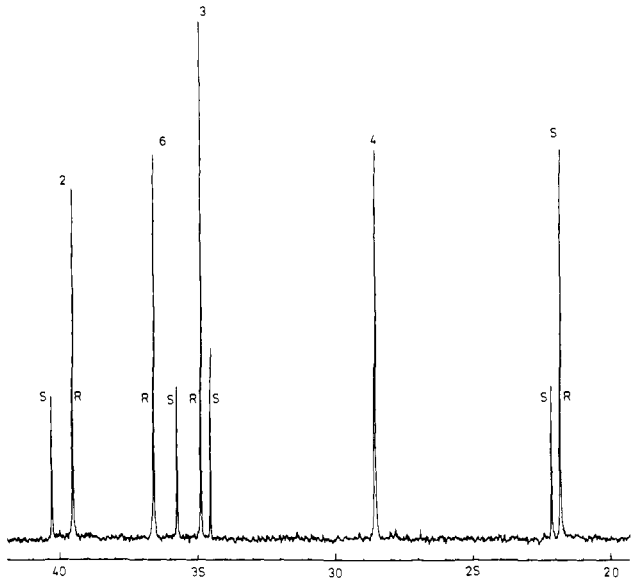

Figure 8. ^{13}C NMR spectrum of the (2*R*,3*R*)-2,3-butanediol acetals of 3-(nitromethyl)cyclohexanone and *R*,*S* assignment according to Figure 9.

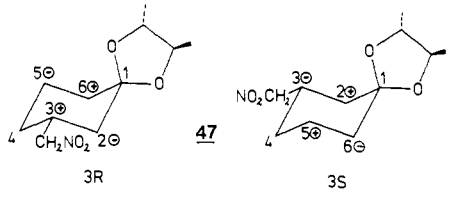

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Figure 9. Assignment of the absolute configuration to both enantiomers of **45** after acetalization with (2*R*,3*R*)-2,3-butanediol and fitting the acetals in the model (Figure 1).

The above formulated rule is only valid for six-membered-ring ketones whose preferred conformation in the acetals is the chair form. A few examples collected in Table III indeed demonstrate that our rule cannot be used for acyclic ketones, cyclopentanones, and cycloheptanones and for cyclohexanones and cyclohexenones mainly consisting in boat or twist conformations.

1.5. Determination of the Absolute Configuration. Since the empirical rule illustrated above turns out to hold for all six-membered-ring ketones having a given chair form as the preferred conformation in the acetals, it can be used to determine the absolute configuration of such chiral ketones. This will be shown for some enantiomerically enriched 3-(1-nitroalkyl)cyclohexanones which were recovered from HLAD-catalyzed reductions of the racemic ketones.[21]

In the ^{13}C NMR spectra of the acetals of such reaction residues (Table IV), always one set of more intense and one set of less intense signals are found, corresponding with the acetals of the major enantiomer and the minor enantiomer of these ketones, respectively (Figure 8).

In Figure 9 both acetals of 3-(nitromethyl)cyclohexanone are shown after superposition with the model (Figure 1). This shows that in the doublet[22] corresponding with the diastereotopic carbon atoms 2, the signal with the lower δ value has to be assigned to the 3*R* enantiomer and the signal with the higher δ value to the 3*S* enantiomer. Analogously, in the doublet from C-5, the signal with the lower δ value has to be assigned to the 3*R* and the one with the higher δ value to the 3*S* enantiomer. Futhermore, in the doublets from C-3 and C-6 the lower δ value corresponds with the 3*S* enantiomer and the higher one with the 3*R* enantiomer. In each of these four cases the more intense signal of a doublet

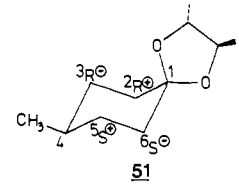

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Figure 10. (2*R*,3*R*)-2,3-Butanediol acetal of **49** fitted in the model (Figure 1).

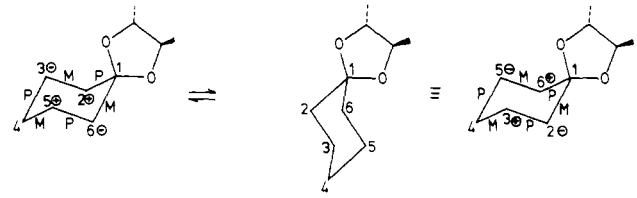
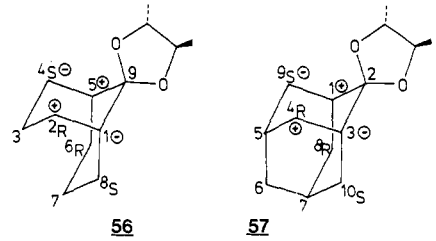


Figure 11. Both equivalent chair conformations of **53** acetalyzed with (2*R*,3*R*)-butanediol and fitted in the model (Figure 1).



56 **57**

Figure 12. (2*R*,3*R*)-2,3-Butanediol acetals of **54** and **55** fitted in the model (Figure 1).

is assigned to the 3*R* enantiomer and the less intense to the 3*S* enantiomer, which clearly shows that the major enantiomer has a 3*R* configuration. An analogous analysis can be done for all 3-(1-nitroalkyl)cyclohexanones in Table IV.

The absolute configurations of the enzymatically prepared 3-(1-nitroalkyl)cyclohexanones have not been confirmed by a different method. However, all existing models for HLAD-catalyzed stereoselective oxidoreduction reactions[23,24] predict that only (3*S*)-ketones are reactive, so that the 3*R* configuration of the residual ketone is virtually certain.

2. Achiral Six-Membered-Ring Ketones. The ^{13}C NMR spectra of the (2*R*,3*R*)-2,3-butanediol acetals of achiral six-membered-ring ketones, such as cyclohexanone, 4-substituted cyclohexanones, bicyclo[3.3.1]nonan-9-one, and adamantanone, can also be interpreted by the rule developed here. This means an extension of the scope of this rule to carbon atoms which are diastereotopic by internal comparison.[18] The ^{13}C δ values of such acetals are collected in Table V.

In the acetals of 4-substituted cyclohexanones, C-2 and C-6 as well as C-3 and C-5 are diastereotopic by internal comparison and can give rise to a doublet. As shown in Figure 10 for 4-methylcyclohexanone (**51**), the empirical rule predicts that in the doublet corresponding with C-2 and C-6, the signal with the lower δ value has to be assigned to the *pro-S* carbon atom and the signal with the higher δ value to the *pro-R* carbon atom.[26] Analogously, in the doublet of C-3 and C-5 the signal with the higher δ value has to be assigned to the *pro-S* and the signal with lower δ value to the *pro-R* carbon atoms. The ring carbon atoms of the other 4-substituted acetals (**52–54**) can be assigned in an analogous way. The peak distance of the doublets ($\Delta\Delta\delta$) of these products varies considerably and will be discussed later.

The acetal of cyclohexanone **55** is a conformationally flexible system, and the cyclohexanone ring exists in two equivalent chair conformations. Both C-2 and C-6 can occupy the + position as

(21) Van Elsacker, P. Ph.D. Thesis, in progress.
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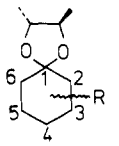
(26) Hanson, K. R. *J. Am. Chem. Soc.* **1966**, *88*, 2731.

Table I. ^{13}C δ Values of Chiral Cyclohexanones Acetalized with (2*R*,3*R*)-2,3-Butanediol



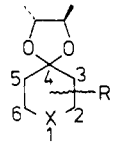
compd no., R[a] =		^{13}C δ values of the ring C atoms						
		I, C-1	II, C-2	III, C-3	IV, C-4	V, C-5	VI, C-6	ref
1a, 2-CH_3	2*S*	110.10	39.64	32.21	24.95	23.79	37.23	*b*, *c*
1b, 2-CH_3	2*R*	110.10	40.42	32.11	24.95	24.20	36.53	
2a, 2-CH_2CH_3	2*S*	110.07	46.79	28.26	24.84	23.67	37.29	5
2b, 2-CH_2CH_3	2*R*	110.34	47.46	28.19	24.84	24.16	36.62	
3a, 2-$CH_2CH_2CH_3$	2*S*	110.0	44.5	28.6[d]	24.7[d]	23.6[d]	37.1	6
3b, 2-$CH_2CH_2CH_3$	2*R*	110.0	45.2	28.6[d]	24.7[d]	24.1[d]	36.5	
4a, 2-*n*-$C_{10}H_{21}$	2*S*	109.8	44.8	28.1[d]	24.8[d]	23.5[d]	37.2	*e*
4b, 2-*n*-$C_{10}H_{21}$	2*R*	109.8	45.5	28.1[d]	24.8[d]	23.5[d]	36.6	
5a, 2-CH_2Ph	2*R*	109.5	46.9	28.1[d]	24.8[d]	23.6[d]	37.4	6
5b, 2-CH_2Ph	2*S*	109.5	47.6	28.1[d]	24.8[d]	24.1[d]	36.6	
6a, 2-$CH_2CH_2OCH_3$	2*R*	109.8	41.7	28.6[d]	24.6[d]	23.5[d]	37.0	*f*
6b, 2-$CH_2CH_2OCH_3$	2*S*	109.8	42.4	28.6[d]	24.6[d]	24.0[d]	36.4	
7a, 3-CH_3	3*R*	108.49	44.98	30.61	34.07	23.05	36.89	*b*, *g*
7b, 3-CH_3	3*S*	108.49	45.91	30.12	34.07	23.44	35.82	
8a, 3-$C(CH_3)_3$	3*R*	108.97	37.48	45.22	26.02	23.00	36.99	*b*
8b, 3-$C(CH_3)_3$	3*S*	108.97	38.45	44.69	26.02	23.44	35.91	
9a, 3-$COOCH_3$	3*R*	106.85	38.01	40.69	27.29	21.93	36.19	4
9b, 3-$COOCH_3$	3*S*	106.85	38.87	40.21	27.29	22.23	35.21	
10a, 3-$COOCH(CH_3)_2$	3*R*	107.52	38.38	41.61	27.84	22.48	36.67	4
10b, 3-$COOCH(CH_3)_2$	3*S*	107.52	39.29	41.06	27.84	22.78	35.76	
11a, 3-$COO(CH_2)_4CH_3$	3*R*	106.79	37.89	40.89		22.23	36.12	4
11b, 3-$COO(CH_2)_4CH_3$	3*S*	106.79	38.80	40.27		22.23	35.15	
12a, 3-CN	3*R*	105.56	38.61	26.22	28.46	21.79	35.87	3
12b, 3-CN	3*S*	105.56	39.55	25.86	28.46	22.20	35.00	
13a, 3-SPh	3*R*	107.85	43.26	43.76	32.85	23.00	36.85	7
13b, 3-SPh	3*S*	107.85	44.29	43.26	32.69	23.40	35.88	
14a, 3-SPh-*p*-CH_3	3*R*	107.55	42.60	43.64	32.19	22.42	36.25	14, *h*
14b, 3-SPh-*p*-CH_3	3*S*	107.55	43.64	43.08	32.19	22.81	35.25	
15a, 3-SPh-*p*-$C(CH_3)_3$	3*R*	107.45	42.56	43.27	32.29	22.34	36.16	7, *i*
15b, 3-SPh-*p*-$C(CH_3)_3$	3*S*	107.45	43.57	42.81	32.29	22.73	35.17	
16a, 3-SPh-*p*-Cl	3*R*	107.36	42.45	43.48	32.00	22.37	36.16	7
16b, 3-SPh-*p*-Cl	3*S*	107.36	43.48	42.96	31.88	22.77	35.18	
17a, 3-SPh-*p*-OCH_3	3*R*	107.55	42.56	44.34	32.08	22.34	36.12	7, *j*
17b, 3-SPh-*p*-OCH_3	3*S*	107.55	43.85	43.58	32.08	22.82	35.11	
18a, 3-SPh-*m*-OCH_3	3*R*	107.4	42.5	43.0	32.1	22.4	36.2	7
18b, 3-SPh-*m*-OCH_3	3*S*	107.4	43.5	42.5	32.1	22.8	35.2	
19a, 3-SPh-*o*-OCH_3	3*R*	107.4	42.3	41.2	31.8	22.3	36.1	7
19b, 3-SPh-*o*-OCH_3	3*S*	107.4	43.3	40.6	31.8	22.7	35.2	
20a, 3-S-β-Naph	3*R*	107.6	42.6	43.3	32.2	22.3	36.3	7
20b, 3-S-β-Naph	3*S*	107.6	43.7	42.6	32.0	22.7	35.3	
21a, 3-SCH_2Ph	3*R*	107.20	42.73	40.34	32.01	22.38	36.13	14, *k*
21b, 3-SCH_2Ph	3*S*	107.20	43.77	39.87	32.01	22.73	35.17	
22a, 3-SePh	3*R*	107.98	43.52	38.93	33.10	23.38	36.38	8
22b, 3-SePh	3*S*	107.98	44.56	38.53	33.10	23.69	35.45	
23a, 3-SePh-*p*-CH_3	3*R*	107.71	43.35	38.54	32.90	23.12	36.14	8
23b, 3-SePh-*p*-CH_3	3*S*	107.71	44.39	38.17	32.90	23.47	35.20	
24a, 3-SePh-*p*-Cl	3*R*	107.62	43.31	39.10	32.80	23.11	36.14	8
24b, 3-SePh-*p*-Cl	3*S*	107.62	44.32	38.71	32.71	23.46	35.23	
25a, 3-SPh-*p*-$C(CH_3)_3$-4,4-$(CH_3)_2$	3*S*	107.61	40.59	54.64	34.31	37.69	32.89	7, *l*
25b, 3-SPh-*p*-$C(CH_3)_3$-4,4-$(CH_3)_2$	3*R*	107.61	41.05	54.18	34.12	38.11	32.21	

[a] For ^{13}C δ values of the substituents and of the dioxolane ring, see the original papers mentioned in the column ref. [b] Unpublished results. [c] Substituent: **1a**, 14.44, **1b**, 14.35; dioxolane; 79.83, 79.20, 77.79, 77.54; 18.82, 17.74, 16.25, 16.09. [d] These values are from ref 13; the assignments to the C atoms are ours. [e] Substituent: CH_2, 31.9, 30.2, 29.7, 29.4, 28.8, 28.6, 28.5, 27.5, 22.7; CH_3, 14.1; dioxolane, 79.3, 77.3; 17.9, 16.3. [f] Substituent: CH_2, 29.4; CH_2O, 71.6; OCH_3, 58.0; dioxolane: 78.00, 77.79; 17.16, 17.06, 16.96. [g] Substituent: CH_3, 22.44, 22.33; dioxolane, 78.00, 77.79; 17.16, 17.06, 16.96. [h] Substituent: *p*-CH_3, 20.76. [i] Substituent: *p*-$\underline{C}(CH_3)_3$, 33.99; *p*-$C(\underline{C}H_3)_3$, 30.94. [j] Substituent: *p*-OCH_3, 54.78. [k] Substituent: CH_2, 34.34, 34.41. [l] Substituents: *p*-$\underline{C}(CH_3)_3$, 34.21; *p*-$C(\underline{C}H_3)_3$, 31.11; CH_3, 19.19, 30.03.

well as the − position (Figure 11). C-3 and C-5 can occupy a + or a − position. As a result, at room temperature the ^{13}C NMR spectrum shows a singlet for C-2 and C-6 and for C-3 and C-5, but at −90 °C two doublets are found. In this low-temperature spectrum, the signal with the lower δ value in the doublet of C-2 and C-6 has to be assigned to the carbon atom in the MPM loop[25] and the signal with the higher δ value to the carbon atom in the PMP loop. Analogously, in the doublet of C-3 and C-5, the signal with the higher δ value is assigned to the MPM carbon atom and the signal with the lower δ value to the PMP carbon atom.

The acetal of bicyclo[3.3.1]nonan-9-one (**56**) has C_2 symmetry (Figure 12), and either cyclohexane ring can be superimposed with the model (Figure 1). As a result of the C_2 symmetry, C-1 and C-5 are identical and can occupy the + as well as the − position, and consequently only a singlet is observed in the ^{13}C NMR spectrum. Also C-2 and C-6 are identical, as well as C-4 and C-8, but these pairs of identical atoms are mutually diastereotopic. C-2 and C-6 only occupy the + position and C-4 and C-8 only the − position. A doublet is found in the ^{13}C NMR spectrum. The signal with the higher δ value is assigned to the *pro-R* atoms and the signal with the lower δ value is assigned to the *pro-S* atoms (see footnote *c* of Table V). The ^{13}C NMR spectrum assignment of the (2*R*,3*R*)-2,3-butanediol acetal of adamantanone (**57**) can be done in completely the same way.

Table II. ^{13}C δ Values of Chiral Tetrahydropyran-4-ones and Tetrahydrothiopyran-4-ones Acetalized with (2*R*,3*R*)-2,3-Butanediol



compd no., R[a] =		^{13}C δ values of the ring C atoms						
		I, C-4	II, C-3	III, C-2	IV, X	V, C-6	VI, C-5	ref
26a, 2-CH_3	2*S*	105.85	44.29	71.67	O	65.17	37.53	10
26b, 2-CH_3	2*R*	105.85	45.26	71.38	O	65.38	36.47	
27a, 2-CH_2CH_3	2*S*	106.04	42.21	76.94	O	65.17	37.88	10
27b, 2-CH_2CH_3	2*R*	106.04	43.20	76.59	O	65.41	36.80	
28a, 2-$CH(CH_3)_2$	2*R*	106.35	39.41	78.34	O	65.23	37.98	10
28b, 2-$CH(CH_3)_2$	2*S*	106.35	40.42	77.92	O	65.47	36.91	
29a, 2-Ph	2*R*	105.85	44.24	77.78	O	65.71	37.65	10
29b, 2-Ph	2*S*	105.85	45.26	77.44	O	65.92	36.62	
30a, 2-CH_3	2*S*	106.9	46.6	35.7	S	26.3	37.9	9
30b, 2-CH_3	2*R*	106.9	47.7	35.4	S	26.6	36.7	
31a, 2-CH_2CH_3	2*S*	107.3	44.7	43.0	S	26.2	38.7	9
31b, 2-CH_2CH_3	2*R*	107.3	45.8	42.7	S	26.4	37.5	
32a, 2-$CH(CH_3)_2$	2*R*	107.6	42.0	48.3	S	26.1	38.8	9
32b, 2-$CH(CH_3)_2$	2*S*	107.6	43.1	48.0	S	26.3	37.6	
33a, 2-Ph	2*R*	107.2	45.0	45.1	S	27.7	39.3	9
33b, 2-Ph	2*S*	107.2	46.1	45.0	S	27.9	37.0	
34a, 3-CH_3	3*R*	108.25	41.00	33.51	S	26.84	37.97	11
34b, 3-CH_3	3*S*	108.25	41.75	33.51	S	26.95	37.52	
35a, 3-CH_2CH_3	3*R*	108.32?	47.94	30.16	S	26.56	37.50	11
35b, 3-CH_2CH_3	3*S*	108.49?	48.52	30.16	S	26.74	37.30	

[a] For ^{13}C δ values of the substituents and of the dioxolane ring, see the original papers mentioned in the column ref.

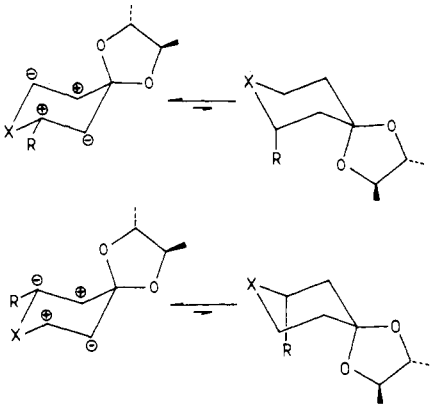


Figure 13. (2*R*,3*R*)-2,3-Butanediol acetals conformationally fixed by 1,3-diaxial interactions.

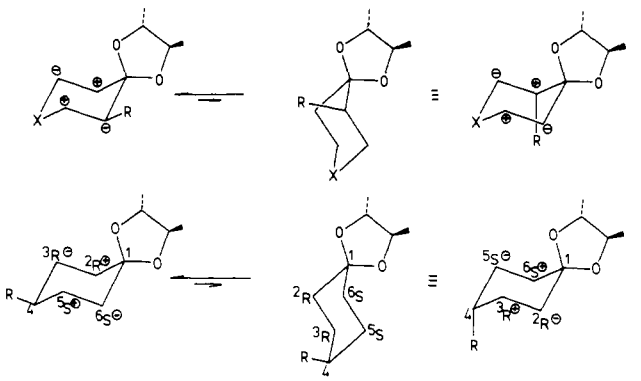


Figure 14. Conformationally mobile (2*R*,3*R*)-2,3-butanediol acetals.

3. Shift Differences, $\Delta\Delta\delta$. In Tables VI–VIII, the values of the shift differences, $\Delta\Delta\delta$, for the diastereotopic carbon atoms of the acetals **1–25**, **26–35**, and **51–57**, respectively, are collected.

It is remarkable that the highest $\Delta\Delta\delta$ values are found for all 3-substituted cyclohexanones and all isosteric six-membered-ring ketones such as 2-substituted tetrahydropyran-4-ones and tetrahydrothiopyran-4-ones and that these values are rather constant. Mean $\Delta\Delta\delta$ values and the variances for C-2, C-3, C-5, and C-6 in the 3-substituted cyclohexanones **7–17** and **21–24** and for the corresponding carbon atoms in the 2-substituted tetrahydropyran-4-ones **26–29** are collected in Table IX.

These high and more or less constant $\Delta\Delta\delta$ values can easily be explained by the conformational stability of all of these acetals. The substituents are virtually in an equatorial position, since a substituent in the axial position experiences a strong 1,3-diaxial interaction with the dioxolane ring (Figure 13). As a result all ring carbon atoms of these acetals are fixed in our model (Figure 1) either on a + or on a − position.

Also, for other rigid structures having carbon atoms fixed on well-defined positions in our model, such as 4-*tert*-butylcyclohexanone (**52**), bicyclo[3.3.1]nonan-9-one (**56**) (Figure 11), adamantanone (**57**), and even cyclohexanone at −90 °C (**55**), $\Delta\Delta\delta$ values are found which are in good agreement with the values in Table IX.

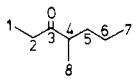
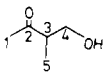
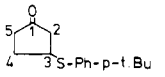
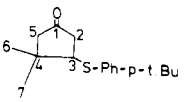
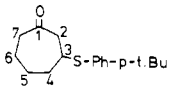
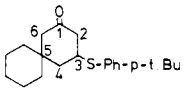
On the other hand all other six-membered-ring ketones which can occur in two chair conformations show lower $\Delta\Delta\delta$ values. Indeed, as can be seen in Figure 14, in such cases ring carbon atoms alternate between + and − positions, the net result being reflected in lower $\Delta\Delta\delta$ values. In the series of 4-substituted cyclohexanones, the $\Delta\Delta\delta$ values decrease for decreasing conformational energies[27] of the substituents. However, a good correlation between the $\Delta\Delta\delta$ values and the equatorial and axial populations, as calculated by the Boltzmann equation from ΔG_x values from the literature,[27] is not found.

As can be seen from Table IX, the two mean $|\Delta\Delta\delta|$ values found for the carbon atoms in the α-position relative to the spiro-carbon atom of the acetals derived from 3-substituted cyclohexanones and 2-substituted tetrahydropyran- and thiopyran-4-ones are almost equal (±1 ppm). This means that the diastereotopic differentiation of these carbon atoms initially comes from the centers of chirality in the dioxolane ring and not from the centers in the substituted ring. Clearly an indirect interaction of the dioxolane ring, most probably via the axial C–H bonds, is responsible for the differentiation of the α-carbon atoms, since all direct interactions with the α-atoms are identical due to the local C_2 axis of the dioxolane ring.

The mean $|\Delta\Delta\delta|$ values found for the β-positions are not equal: 0.47 ppm for the substituted and 0.34 ppm for the unsubstituted

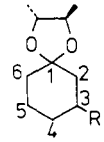
(27) Hirsch, J. A. *Top. Stereochem.* **1967**, *1*, 199.

Table III. ^{13}C δ Values of Chiral Ketones Acetalized with (2*R*,3*R*)-2,3-Butanediol

	(2*R*,3*R*)-2,3-butanediol acetals of		^{13}C δ values[a] of C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	ref
36		4*R*,*S*[b]	7.49 7.49	27.53 27.53	113.31 113.31	40.39 40.14	33.63 33.20	20.96 20.96	14.19 14.19	13.83 13.83	*c*, *d*
37		3*R*,*S*[b]	22.09 21.91	111.01 110.89	43.69 43.60	64.31 64.09	12.07 11.82				19, *e*
38		2*R*,*S*[b]	117.5 117.5	41.77 41.33	31.48 31.05	20.18 20.18	37.43 36.41	13.60 13.11			*c*
39		3*R* 3*S*	117.45 117.45	46.69 46.39	32.6 32.1	32.6 32.6	38.45 37.96	20.22 20.61			*c*
40		3*R* 3*S*	115.86 115.7	45.20 45.0	43.44 43.3	30.93 31.2	37.04 36.6				7, *f*
41		3*S* 3*R*	113.7 113.8	46.9 47.0	56.4 56.4	41.2 41.1	53.7 53.7	27.8 28.1	22.6 23.3		7
42		3*R* 3*S*	109.99 109.55	45.32 45.64	42.22 41.46	35.74 34.51	28.63 26.64	21.95 21.95	40.67 40.67		7, *g*
43		3*R* 3*S*	108.3 108.1	43.2 43.2	39.1 38.7	44.1 44.1	34.9 35.1	45.3 45.3			19
44		1*R* 1*S*	52.09 51.91	116.13 116.01	46.24 46.15	45.01 45.20	*h* *h*	*h* *h*	47.68 47.74	9.32 10.47	19, *h*
45		1*R* 1*S*	45.83 44.88	115.55 115.48	45.52 45.45	35.60 35.79	28.10 28.50	21.97 21.97	37.90 37.57		20
46		1*R* 1*S*	51.27 51.27	117.56 117.56	41.87 41.87	41.00 40.70	139.93 139.52	133.16 133.62	48.82 49.17		20

[a] For ^{13}C δ values of the substituents and of the dioxolane ring, see the original papers mentioned in the column ref. [b] Racemates. [c] Unpublished results. [d] Dioxolane: 78.95, 78.64, 78.52; 16.88. [e] Dioxolane: 78.58, 78.34, 77.53, 77.26; 16.75, 16.69, 15.83 (2C). [f] Substituent: *p*-$\underline{C}(CH_3)_3$, 34.18; *p*-C($\underline{CH}_3$)$_3$, 31.09. [g] Substituent: *p*-$\underline{C}(CH_3)_3$, 34.23; *p*-C($\underline{CH}_3$)$_3$, 31.12. [h] Assignment to either C-5 or C-6 was not possible. 1*S*: 29.35, 27.02, 1*R*: 28.85, 26.67. Bridge methyls: 1*R*, 20.32, 20.22; 1*S*, 20.43, 20.32. Dioxolane: 1*R*, 78.68, 76.74; 17.38, 16.05; 1*S*, 77.96, 77.66; 17.38, 16.28.

Table IV. ^{13}C δ Values and Configuration Assignment of Enzymatically Prepared Chiral 3-(1-Nitroalkyl)cyclohexanones Acetalized with (2*R*,3*R*)-2,3-Butanediol[21]



compd no., R =		^{13}C δ values of the ring C atoms I, C-1	II, C-2	III, C-3	IV, C-4	V, C-5	VI, C-6	assigned to
47,[a] CH_2NO_2	major	107.16	39.51	34.92	28.55	21.87	36.61	3*R*
	minor	107.16	40.28	34.57	28.55	22.19	35.77	3*S*
48,[b] $CHNO_2CH_3$	major	107.4	38.95[c] 38.11	40.05	27.90[c] 27.00	22.22[c] 21.97	36.73[c] 36.70	3*R*
	minor	107.4	39.82[c] 39.11	39.67[c] 39.63	27.90[c] 27.00	22.54[c] 22.38	35.77	3*S*
49,[d] $CHNO_2CH_2CH_3$	major	107.34	38.78	39.10	27.84	22.29[c] 21.91	36.74	3*R*
	minor	107.34	39.77[c] 39.64	38.70[c] 38.66	27.84	22.61[c] 22.34	35.80	3*S*
50,[e] $CNO_2(CH_3)_2$	major	107.77	37.40	44.95	26.26	22.42	36.80	3*R*
	minor	107.77	38.44	43.86	26.26	22.84	35.76	3*S*

[a] Substituent: CH_2NO_2, 80.53; dioxolane, 77.85, 16.51. [b] Substituent: $CHNO_2$, 87.66; CH_3, 16.27; dioxolane; 78.28, 78.18; 16.87. [c] The additional chiral center in the nitroalkyl substituent causes further splitting of these signals. [d] Substituent: $CHNO_2$, 95.10; CH_2, 24.06; CH_3, 10.42; dioxolane, 78.34, 78.10; 16.94. [e] Substituent: CNO_2, 91.26; CH_3, 23.03; dioxolane, 78.22, 78.10; 16.94.

carbon atoms. Here the centers of chirality in the substituted ring clearly have an additional effect on the diastereotopic differentiation.

The spiro atom and the γ-atom are hardly differentiated. This is easily understood by considering that these atoms lie on the 2-fold axis and in a "quasi-mirror plane" of the dioxolane ring,

Table V. ^{13}C δ Values of Achiral Cyclohexanone Derivatives Acetalized with (2*R*,3*R*)-2,3-Butanediol

(2*R*,3*R*)-2,3-butanediol acetals of	^{13}C δ values of the ring C atoms C-1	C-2/6	C-3/5	C-4	assigned to	other signals
51, 4-methylcyclohexanone	108.10	35.87	32.39	31.50	*pro-S* side[a]	4-Me, 21.64;
		36.75	32.02		*pro-R* side[a]	dioxolane, 78.08, 77.83; 17.16, 17.06
52, 4-*tert*-butylcyclohexanone	108.05	36.50	24.95	47.32	*pro-S* side[a]	4-*t*-Bu, 32.31, 27.73; dioxolane, 78.03, 77.79; 17.16
		37.48	24.56			
53, 4-hydroxycyclohexanone	107.09	32.83	31.62	67.62	*pro-S* side[a]	dioxolane, 77.67; 16.69
		33.14	31.43		*pro-R* side[a]	
54, 4-acetoxycyclohexanone	106.42	32.47	27.78	69.81		4-Ac, 169.72, 20.65; dioxolane, 77.61; 16.45
55, cyclohexanone						
$CDCl_3$, room temp	107.70	36.61	23.57	24.97		dioxolane, 77.55; 16.69
CD_3OD, room temp.	109.07	37.97	24.82	26.34		dioxolane, 79.16; 17.38
CD_3OD, −90 °C		37.01	25.00	26.10	MPM side[b]	
		38.28	24.57		PMP side[b]	

(2*R*,3*R*)-2,3-butanediol acetals of	^{13}C δ values of the ring C atoms C-9	C-1/5	C-2,6/4,8	C-3/7	assigned to	other signals
56, bicyclo[3.3.1]nonan-9-one	109.78	37.59	29.36	20.65	*pro-R*[c]	dioxolane, 77.37; 17.12
			29.00		*pro-S*[c]	

(2*R*,3*R*)-2,3-butanediol acetals of	^{13}C δ values of the ring C atoms C-2	C-1/3	C-4,8/9,10	C-5/7	assigned to	other peaks
57, adamantanone	110.30	38.14	35.15	27.05	*pro-R*[d]	C-6, 37.34;
			34.54		*pro-S*[d]	dioxolane, 77.92; 17.42

[a] *pro-R* or *pro-S* to C-4; see Figure 10 and ref 26. [b] See Figure 11 and ref 16, p 409. [c] C-2, *pro-R* to C-1; C-4, *pro-S* to C-5; C-6, *pro-R* to C-5; C-8, *pro-S* to C-1; see Figure 12 and ref 26. [d] C-4, *pro-R* to C-3; C-8, *pro-R* to C-1; C-9, *pro-S* to C-1; C-10, *pro-S* to C-3; see Figure 12 and ref 26.

Table VI. ΔΔδ Values of Chiral Cyclohexanones Acetalized with (2*R*,3*R*)-2,3-Butanediol

	ΔΔδ values[a] of the ring C atoms C-2	C-3	C-5	C-6
1	−0.78	+0.10	−0.41	+0.70
2	−0.67	+0.07	−0.49	+0.67
3	−0.7	0.0	−0.5	+0.6
4	−0.7	0.0	0.0	+0.6
5	−0.7	0.0	−0.5	+0.8
6	−0.7	0.0	−0.5	+0.6
7	−0.93	+0.49	−0.39	+1.07
8	−0.97	+0.53	−0.44	+1.08
9	−0.86	+0.48	−0.30	+0.98
10	−0.91	+0.55	−0.30	+0.91
11	−0.91	+0.62	0.00	+0.97
12	−0.94	+0.36	−0.41	+0.87
13	−1.03	+0.50	−0.40	+0.97
14	−1.04	+0.56	−0.39	+1.00
15	−1.01	+0.46	−0.39	+0.99
16	−1.03	+0.52	−0.40	+0.98
17	−1.29	+0.76	−0.48	+1.01
18	−1.0	+0.5	−0.4	+1.0
19	−1.0	+0.6	−0.4	+0.9
20	−1.1	+0.7	−0.4	+1.0
21	−1.04	+0.47	−0.35	+0.96
22	−1.04	+0.40	−0.31	+0.93
23	−1.04	+0.37	−0.35	+0.94
24	−1.01	+0.39	−0.35	+0.91
25	−0.46	+0.46	−0.58	+0.68

[a] ΔΔδ = δ(**a** diastereoisomer) − δ(**b** diastereoisomer); see Table I.

Table VII. ΔΔδ Values of Chiral Tetrahydropyran-4-ones and Tetrahydrothiopyran-4-ones Acetalized with (2*R*,3*R*)-2,3-Butanediol

	ΔΔδ values[a] of the ring C atoms C-3	C-2	C-6	C-5
26	−0.97	+0.29	−0.21	+1.07
27	−0.99	+0.35	−0.24	+1.08
28	−1.01	+0.42	−0.24	+1.07
29	−1.02	+0.34	−0.21	+1.03
30	−1.1	+0.3	−0.3	+1.2
31	−1.1	+0.3	−0.2	+1.2
32	−1.1	+0.3	−0.2	+1.2
33	−1.1	+0.4	−0.2	+1.3
34	−0.75	0.00	−0.11	+0.45
35	−0.58	0.00	−0.18	+0.20

[a] ΔΔδ = δ (**a** diastereoisomer) − δ (**b** diastereoisomer); see Table II.

Table VIII. ΔΔδ Values of Achiral Cyclohexanone Derivatives Acetalized with (2*R*,3*R*)-2,3-Butanediol

	ΔΔδ values[a] of α-C	β-C
51	0.88	0.37
52	0.98	0.39
53	0.41	0.19
54	0.00	0.00
55	1.27	0.43
56	0.00	0.36
57	0.00	0.61

[a] See Table V.

Table IX. Mean Shift Differences, ΔΔδ, and Variances, *s*

C-nr[a]	ΔΔδ[b]	*s*[b]
2(3)	−1.00	0.09
3(2)	+0.47	0.12
5(6)	−0.34	0.08
6(5)	+0.99	0.07

[a] Cyclohexanones (tetrahydropyran- or -thiopyran-4-ones). [b] Calculated from ΔΔδ values of **7–17**, **21–24**, and **26–29**; see Tables VI and VII.

respectively, and do not experience much of the molecular chirality.

For all ketones having a more flexible skeleton, the ΔΔδ values reflect the mean of the interactions of the dioxolane ring with several conformations of the ketone, which generally results in small ΔΔδ values.

Conclusion

In ^{13}C NMR spectroscopy the stereodifferentiation of carbon atoms of ketones, converted to the (2*R*,3*R*)-2,3-butanediol acetals, is strongly determined by the interactions with the centers of chirality in the dioxolane ring. As a result, all ketones occurring in a well-defined conformation after acetalization, such as six-membered-ring ketones in chair conformation, show the same type of diastereotopic splitting of the ^{13}C NMR signals. This stereodifferentiation is almost independent of the ring substitution and of the presence of heteroatoms in that ring. This can be visualized by fitting the acetals into the model in Figure 1 and can be formulated as follows: "For each pair of diastereotopic ring carbon atoms (by internal or by external comparison[18]) the carbon atom coinciding with a + position in the model has a higher chemical shift than the one coinciding with a − position."

Consequently, this rule can now be used for the determination of the absolute configuration of chiral six-membered-ring ketones from the ^{13}C NMR spectra of their (2*R*,3*R*)-2,3-butanediol acetals. This is an important extension of a method which was primarily elaborated for the determination of the enantiomeric excess of chiral ketones.[12]

Acknowledgment. We are very indebted to Prof. G. Snatzke, who confirmed very recently the 3*R* configuration of the 3-(1-nitroalkyl)cyclohexanones **47**, **49**, and **50** (Table IV) from the CD spectra.

Registry No. (4*R*)-**36** acetal, 105969-74-2; (4*S*)-**36** acetal, 105969-76-4; (2*R*)-**38** acetal, 105969-75-3; (2*S*)-**38** acetal, 106034-29-1; (3*R*)-**39** acetal, 106034-27-9; (3*S*)-**39** acetal, 106034-28-0; (3*R*)-**47**, 105969-77-5; (3*S*)-**47**, 106034-30-4; **48**, 105969-78-6; **49**, 105969-79-7; (3*R*)-**50**, 105969-80-0; (3*S*)-**50**, 106034-31-5; **51**, 106034-32-6; **52**, 106034-33-7; **53**, 105969-81-1; **55**, 106034-34-8; **56**, 105969-82-2; **57**, 105969-83-3.

Theoretical Study of the Photodecomposition of *s*-Triazine

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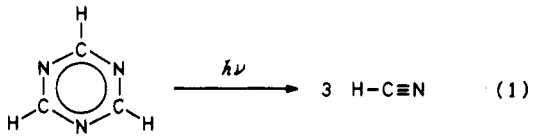
Abstract: The reaction mechanism of the photodissociation of *s*-triazine $C_3H_3N_3$ is examined with the ab initio molecular orbital method. The decomposition which leads to three equivalent HCN molecules is a symmetry-allowed reaction in the ground state under the C_{3h} symmetry, and the symmetric transition state is found to be a true transition state. The activation energy is estimated to be ca. 100 kcal/mol. In the excited states, all low-lying states increase the energies along the reaction coordinate. This means that the electronically excited *s*-triazine must experience the radiationless transition to the ground state and decompose synchronously. We can conclude that the triple dissociation of *s*-triazine occurs on the potential surface of the ground state and is a one-step concerted reaction.

I. Introduction

s-Triazine $C_3H_3N_3$ is a high-symmetry species with aromaticity like benzene. It is, however, known that *s*-triazine easily decomposes by photolysis. *s*-Triazine behaves very differently in photochemical processes compared with the complexity in the case of benzene. While various isomerization processes take place in the excited states of benzene, *s*-triazine simply decomposes to three HCN molecules.



(1)

Ondrey and Bersohn measured the kinetic energies of HCN fragments by laser pulse photolysis at two different wavelength.[1] There is a kind of paradoxical result, where HCN molecules have an average kinetic energy of 10 kcal/mol when they use 248-nm light, while in the case of higher energy excitation, i.e., 198 nm, they observed the translational energy of only 2 kcal/mol. At the same time, Goates, Chu, and Flynn observed the vibrationally excited products HCN by infrared fluorescence spectroscopy.[2]

Since the decomposition reaction 1 seems to be very simple compared with many photodissociation reactions,[3] there are still remaining questions on the mechanism, e.g., whether *s*-triazine decomposes to three HCN molecules simultaneously or step wisely. It is obvious that the energy used in this photodecomposition (115-148 kcal/mol) is not enough to break three CN bonds at one time.

It is very interesting to explore the reaction mechanism and energetics for this photodissociation theoretically. We have applied the ab initio molecular orbital method to investigate the potential energy surfaces of *s*-triazine in the ground and excited states. The equilibrium geometries and the structure of the transition state in the ground state are determined by using the analytical energy gradient method.[4] The excitation energies are evaluated with configuration interaction method.

II. Synchronous Decomposition Pathway in the Ground State

In order to explore the possibility of the triple dissociation of *s*-triazine to produce three equivalent HCN molecules, one can apply the conservation rule of the orbital symmetries to find out the continuity of the electronic structure during the reaction.[5] Assuming the least motion pathway which keeps C_{3h} symmetry, one can find that all occupied orbitals of *s*-triazine smoothly correlate to the linear combination of three HCN molecular orbitals. This means that the triple dissociation is a symmetry-allowed reaction in the ground state. As a result of searching the geometry of the transition state under the C_{3h} symmetry, we obtain the structure shown in Table I.

Table I summarizes the geometries of equilibrium structure and the transition state determined by using the various types of basis sets.[6] In order to confirm whether the calculated structure is a true transition state or not, we have performed the vibrational analysis. As shown in Table II, we find that the force constant of the symmetric structure has only one imaginary frequency. This reveals the existence of the concerted reaction pathway although the energy barrier is high. It is noticeable that the decomposition of *s*-triazine in the ground state is the one-step reaction via symmetric transition state, and this reaction obeys the Woodward-Hoffmann rule. The activation energy corrected by the zero-point vibration energy is calculated to be 110 kcal/mol within the theory of SCF level by using the 6-31G** basis set. Since the effect of electron correlation would reduce the energy at the transition state, we estimate the barrier height to be ca. 100 kcal/mol.

Figure 1b shows the normal coordinate for the imaginary frequency at the transition state. This nuclear motion clearly shows that the H-C-N bending mode will be excited in HCN

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