Crystal Structure of 1,2-Diphenyl-5,7-di-*tert*-butylspiro[2.5]octa-1,4,7-trien-6-one, a Possible Model for Diphenylvinylidenephenonium Ions

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The structure of the title compound was determined by X-ray analysis. It was found that the cyclopropenyl and the cyclohexadienyl moieties are perpendicular. The C–C–C angle at the spiro atom is 49.64(7)°, one of the smaller known for an sp³ carbon. The structure of the cyclohexadienone moiety was analyzed by comparing the C=O distance to the C–C and C=C distances. Using data from previously determined structures, it was found that the spiro annelation has no extraordinary effect on the structure of this moiety. Ab initio calculations at B3LYP/6-31G* and MP2/6-31G* levels and NRT analysis were used to analyze the structure of the title compound and its relevance as a model for vinylidenephenonium ions. We conclude that the neutral spirotrienone is not a good model for the charged bridged ion.

Introduction

Aryl-substituted vinylidenephenonium ions, e.g., **1** (where Ar^{2+} is the positively charged moiety of the phenonium ion derived from Ar^2), are intermediates in 1,2-aryl rearrangements across the double bond of vinyl cations, e.g., **2**.[1] However, although calculations show that **1** sometimes reside in local minima,[2] these species are nearly always higher in energy than the less strained open ions **2**. The limited experimental evidence for the existence of vinylidenephenonium ions is indirect, involving the stereochemical outcome of the solvolysis of β-aryl-substituted vinylic systems carrying an α leaving group.[3] However, no direct experimental evidence for the structure of a vinylidenephenonium ion is available.
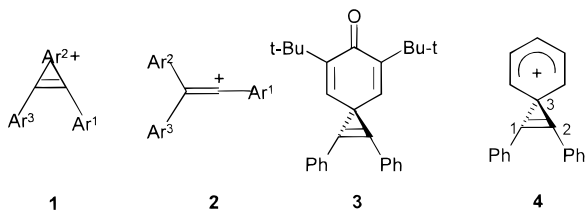
[2.5]octa-1,4,7-trien-6-one system. The cyclohexadienone moiety resembles the phenonium ion moiety with the exception that the delocalized positive charge in the latter is replaced by the partial positive charge on the carbon of the carbonyl group. Whether, despite this difference, the spiro derivative is still a good model for **1** is unknown.

A family of 1,2-disubstituted-5,7-di-*tert*-butylspiro[2.5]octa-1,4,7-trien-6-ones was prepared by vinylic solvolysis reactions and studied by Kobayashi, Taniguchi, and co-workers.[4] Because several of these compounds are unstable, we have taken the 1,2-diphenyl derivative **3**[4c] as a model for a 1,2-diphenylvinylidenephenonium ion, **4**. We were able to obtain crystals suitable for X-ray crystallography, and the crystallographic data are given below and compared with calculated data for the parent 1,2-diphenylvinylidenephenonium ion.[2b]

In addition to the interest in the carbocationic nature of **3**, there is also a crystallographic interest in its cyclopropenyl moiety. The geometry of the strained cyclopropyl unit is usually very sensitive to substituent effects that cause additional strain and/or distortions by conjugation.[5] This sensitivity is even more pronounced for the cyclopropenyl group, where there is a tendency toward shortening of the double bond and lengthening of the single bonds on substitution with electron-withdrawing groups in the 3-position. Cyclopropyl conjugation plays a role similar to that demonstrated in a detailed structural investigation of unsaturated substituents at the cyclopropyl group, including spiroconnected

A possible, experimentally accessible neutral model for a bridged vinylidenephenonium cation might be the spiro-

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(1) (a) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic Press: New York, 1979; Chapter 6. (b) *Dicoordinated Carbocations*; Rappoport, Z., Stang, P. J., Eds.; Wiley: New York, 1997; especially chapter 7.
(2) (a) Apeloig, Y.; Franke, W.; Rappoport, Z.; Schwarz, H.; Stahl, D. *J. Am. Chem. Soc.* **1981**, *103*, 2770. (b) Yamataka, H.; Biali, S. E.; Rappoport, Z. *J. Org. Chem.* **1998**, *63*, 9105. (c) Yamataka, H., unpublished results.
(3) Stang, P. J.; Dueber, T. E. *J. Am. Chem. Soc.* **1973**, *95*, 2683, 2686; **1977**, *99*, 2602.

(4) (a) Ohba, H.; Ikeda, T.; Kobayashi, S.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1980**, 988. (b) Ikeda, T.; Kobayashi, S.; Taniguchi, H. *Synthesis* **1982**, 393. (c) Ikeda, T.; Kobayashi, S.; Taniguchi, H. *Chem. Lett.* **1982**, 387, 391.
(5) (a) Tidwell, T. T. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; John Wiley: Chichester, 1987; pp 565–632. (b) Rozsondai, B. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; John Wiley: Chichester, 1995; Vol. 2, Chapter 3, pp 139–221.

groups.[6] For the cyclopropenyl group, the shortest significant[7,8] experimentally determined double bonds are those of 3-ethenylcyclopropene[9] (**5**) [C=C 1.279(1), C—C 1.517(1) Å, C(1)—C(3)—C(2) 50.1(1)°] and 3-ethynylcyclopropene[10] (**6**) [C=C 1.255(2), C—C 1.501(2) Å, C(1)—C(3)—C(2) 49.4(1)°]. In both cases, the double bond is shortened in comparison with that in the parent cyclopropene (**7**) [determined by microwave spectra: C=C 1.2954(4), C—C 1.509(1) Å],[11] and in **5** the ring single bond is also lengthened. The difference between C—C bond lengths in cyclopropanes increases from 0.015 Å in ethynylcyclopropane (**8**) to 0.025 Å in 1,1-diethynylcyclopropane (**9**) to 0.028 Å in dispiro[2.2.2.2]deca-4,9-diene (**10**).[6]

5: R = HC=CH$_2$
6: R = C≡CH
7: R = H

8: R = H
9: R = C≡CH

10
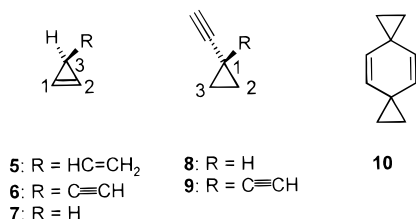
Results and Discussion

We expected some unusual features in 1,2-diphenyl-5,7-di-*tert*-butylspiro[2.5]octa-1,4,7-trien-6-one (**3**), in terms of strain and conjugation, for three reasons: (a) There may be some through-space interactions between the π-systems of the phenyl rings and the cyclopropenyl double bond. (b) There should be some cyclopropyl conjugation between the cyclopropene Walsh-orbitals and the double bonds of the cyclohexadiene fragment. (c) There should be some rehybridization of C(3) due to a zwitterionic contribution from the carbonyl group. Feature (a) predicts, provided that the phenyl rings are almost coplanar with the three-membered ring, a lengthening of the cyclopropenyl double bond and no significant change in the adjacent C—C bonds in the three-membered ring. Feature (b) also predicts that the cyclopro-

(6) Haumann, T.; Boese, R.; Kozhushkov, S. I.; Rauch, K.; de Meijere, A. *Liebigs Ann./Recueil* **1997**, 2047.

(7) The criteria for significance of X-ray structural data are difficult to classify, although attempts have been made by the Cambridge Crystallographic Data Centre (CCDC). For carbon atoms that are linked by double or triple bonds, we prefer to restrict ourselves to the inclusion of high-angle data (2Θ ≥ 60° for Mo radiation) because otherwise, in the standard refinement procedures, the distances tend to become too short. This is easily explained by the fact that the refinement procedure of (spherical) atoms tries to shift the atoms together so that the bonding electron density is "absorbed" and a minimum residual electron density results. Low-temperature experiments with a higher localization of electron densities and high-angle data with the higher contribution of core electrons will avoid such an artifact. However, it should be noted that the inclusion of the high-angle data, which are weaker and therefore measured with a lower accuracy, produce higher *R*-values. In contrast, low-temperature experiments (e.g., *T* < 150 K) tend to give longer intramolecular distances, which is a different artifact, but can be roughly corrected (see Dunitz, J. D. *Angew. Chem.* **1988**, *100*, 910; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 880). This kind of correction gives a lengthening of 0.001−0.002 Å for **3**.

(8) The records for the shortest C=C double bond of 1.394(3) Å and the smallest angle at an sp^3 carbon atom of 50.71(1)° were claimed for 2-*p*-chlorophenyl-3,3-dimethyl-1-methoxycyclopropene (Søtofte, I.; Crossland, I. *Acta Chem. Scand.* **1989**, *43*, 168), which fulfills nonspecified significance criteria, see: *Chemie-Rekorde*; Quadbeck-Seeger, H.-J., Ed.; Wiley-VCH: Weinheim, 1997; p 178.

(9) Boese, R.; Bläser, D.; Billups, W. E.; Haley, M. M.; Luo, W.; Arney, B. J., Jr. *J. Org. Chem.* **1994**, *59*, 8125.

(10) Baldridge, K. K.; Biggs, B.; Bläser, D.; Boese, R.; Gilbertson, R. D.; Haley, M. M.; Maulitz, A. H.; Siegel, J. S. *Chem. Commun.* **1998**, 1137.

(11) Stigliani, W. M.; Laurie, V. W.; Li, J. C. *J. Chem. Phys.* **1975**, *63*, 1890.
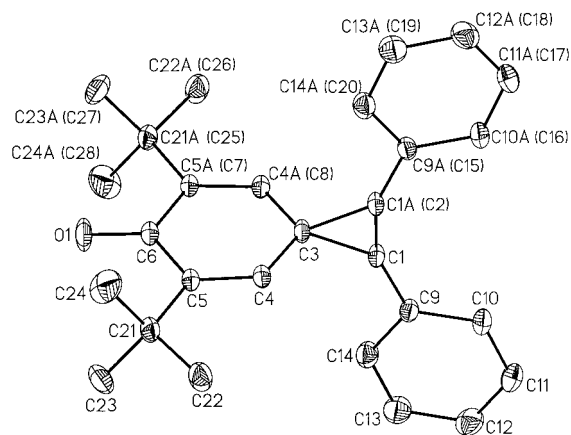

Figure 1. Ellipsoid presentation (50%) of **3**. Important distances (Å) and angles (deg); see footnote 13 for definition: C(1)—C(2) 1.297(2), C(1)—C(3) 1.545(1), C(3)—C(4) 1.460(1), C(4)—C(5) 1.349(1), C(5)—C(6) 1.491(1), C(6)—O(1), 1.237(1), C(1)—C(9) 1.438(1), C(9)—C(10) 1.402(1), C(10)—C(11) 1.387(1), C(11)—C(12) 1.389(2), C(12)—C(13) 1.391(2), C(13)—C(14) 1.387(1), C(9)—C(14) 1.397(1); C(1)—C(3)—C(2) 49.64(7), C(3)—C(1)—C(2) 65.18(4), C(4)—C(3)—C(8) 116.47(9), C(3)—C(4)—C(5) 123.59(8), C(4)—C(5)—C(6) 118.67(8), C(5)—C(6)—C(7) 118.97(10).

penyl double bond will be lengthened. In addition, a lengthening of the adjacent C—C bonds is expected, when compared to cyclopropane derivatives, especially when comparing **10** [bond length of the spiro cyclopropyl bond 1.526(1) Å] to the respective bond in 1,1-diethenylcyclopropane [1.524(1) and 1.515(1) Å in the two rotational isomers of the compound].[12] The effect of feature (c) is to shorten the cyclopropenyl double bond, in agreement with the observation that electron-withdrawing groups at the spiro atom cause its rehybridization and a lengthening of the adjacent bonds. Consequently, superposition of these effects might lead to a geometry which was not hitherto observed.

The structure determination of **3** (see Experimental Section and Figure 1[13]) indeed revealed some of these features. It has a crystallographic C_2 symmetry, which implies that the cyclopropene and the cyclohexadiene rings are orthogonal to each other, the latter being essentially planar. Both phenyl groups are slightly tilted and adopt an interplanar angle to the cyclopropenyl ring of 9.2°.[14] The *ortho* hydrogen atoms at C(10) and C(16) (bond distances expanded to 1.08 Å) are separated by 2.500 Å.

The double bond length in the cyclopropenyl ring is 1.297(2) Å, the same as in **7**,[9] and because the adjacent single bonds are significantly longer [1.545(1) Å] than in **5** [1.517(1) Å], a smaller angle at the spiro atom [49.64(7)° in **3**, 50.8(1)° in **7**] is obtained. This angle is almost as small as the current "record holder" for an sp^3 carbon atom in a small ring [49.4(1)°],[6] which has a much smaller double bond distance [1.255(2) Å].[6] Quite obviously, features (a) and (c) above seem to work in opposite

(12) Here, one ethynyl group is *synclinal* and the other is *antiperiplanar* to the proximal bonds; see also ref 6.

(13) Because of the symmetry of the molecule, the IUPAC and the CSD numbering schemes are different. Where there are differences, the IUPAC numbering is given in parentheses. The bond lengths and angles here are reported according to the IUPAC scheme.

(14) In the 19 compounds found in the CSD with phenyl rings in the C(1), C(2) positions of a cyclopropene fragment, all of the rings are almost coplanar with the three-membered ring.
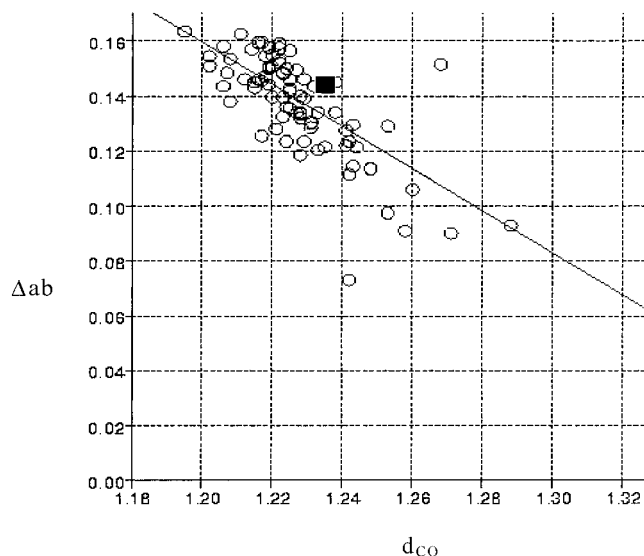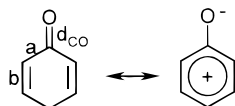
Figure 2. A scatter plot of 84 structures from the CSD with a carbonyl fragment attached at a cyclohexadiene fragment. Δab represents the mean difference of bond distances $a-b$ (Scheme 1), and d_{CO} represents the C=O bond distances. The black square indicates the data for **3**.

Scheme 1. Resonance Representation of Charge Delocalization in Cyclohexa-2,5-dien-1-one


directions for the double bond, whereas for the adjacent bonds, feature (b) dominates.

For assessing effect (c), which transfers some positive charge to the spiro atom, it is beneficial to inspect also the cyclohexadienone ring. The single bond lengths at the spiro atom are 1.460(1) Å, whereas the double bond lengths are 1.349(1) Å, i.e., they are shorter and longer, respectively, than those in the dispiro compound **10**. This result suggests the presence of some conjugation, an effect which should be more pronounced for the double bonds compared with the proximal single bonds [C(5)–C(6) 1.491(1) Å] at the carbonyl group. A contribution of the zwitterionic structure, as shown in Scheme 1, is expected to reduce the difference between the single and double bond lengths ($\Delta = 0.142$ Å) and simultaneously to lengthen the C=O bond [1.237(1) Å]. To find out if the geometry in the cyclohexa-2,5-dienone fragment in **3** reveals some unusual features, we searched related structures in the Cambridge Structural Data Base (CSD). We found 84 structures that contain the cyclohexa-2,5-dienone fragment, are not disordered, have R-values <10%, contain no metal atoms, and have hydrogens or noncyclic bonded carbon atoms in the 2,3,4,5-positions. The C=O distance (d_{CO}) and the difference between the C(1)–C(2) and the C(2)=C(3) bonds (C(5)–C(6) and C(4)=C(5), respectively, in **3**), Δab, were extracted and are given as a scatter plot in Figure 2. For unsymmetrically substituted systems, the mean value of the differences was calculated. Despite the large scatter, there is a rough correlation between d_{CO} and Δab, according to which the longer the C=O distance, with a consequent higher negative charge at the oxygen, the greater is the equalization of the single and double bonds in the cyclohexadiene unit. The point for **3**, marked as a black

block in Figure 2, lies almost perfectly on the linear regression correlation line. However, because of the large scatter, this line should be regarded as representing only a rough trend. The position of the point for **3** reflects a "normal" cyclohexa-2,5-dienone fragment, without an additional positive charge in the ring. Therefore, the dominant effects on the geometry of **3** are (a) and (b), whereas effect (c) contributes to a much lower extent.

To further evaluate the quality of spiro[2.5]octa-1,4,7-trien-6-ones as models for vinyl cations we conducted calculations on the parent spiro compound, spiro[2.5]octa-1,4,7-trien-6-one **11a** and its symmetrical 1,2-divinyl (**11b**), 1,2-dihydroxy (**11c**), and 1,2-dinitro (**11d**) derivatives. Also calculated were the six-membered ring moiety cyclohexa-2,5-dien-1-one (**12**), the parent vinylidenephenonium ion (**13**), and the 1,2-disubstituted cyclopropenes **14**. Data on cation **4** at B3LYP/6-31G* were available

11 a: X = H; **b**: X = H₂C=CH;   **12**   **13**
c: X = OH; **d**: X = NO₂

14 a:X = CH₂=CH;
b: X = OH; **c**: X = NO₂
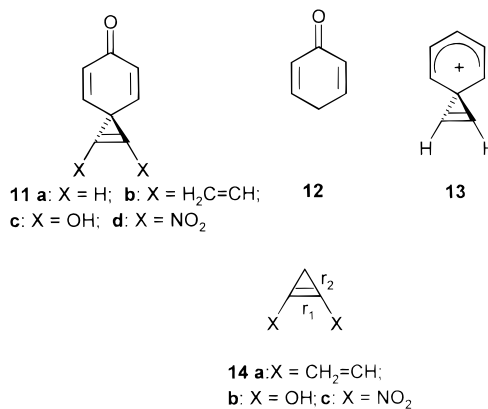
from a previous work.[2b,c] Our calculations were carried out using the Gaussian 94 program,[15] at HF/6-31G*, MP2/6-31G*, and B3LYP/6-31G* levels of theory.[2b] The calculated bond lengths for **11a**–**d**, **4**, **12**, and **13**, together with the experimental data for **3**, are given in Table 1. To assess which are the most suitable theoretical levels for evaluating the experimental results, the differences between the calculated and structural parameters for **11a** and **11b** and **3** were calculated in two ways: (a) The average of the sum of all of the nine experimental CC bond lengths in **3** was subtracted from the average of the sum of the calculated bond lengths. (b) The difference between each of the nine pairs of calculated vs observed CC bond lengths was averaged.[16] The data (Table 2) show the larger differences for the HF/6-31G* values, suggesting that this is an inadequate method for estimating the geometries. The difference between B3LYP/6-31G* and MP2/6-31G* is not large, the

(15) *Gaussian 94* and *G94w*, Revision E.1; Frischm, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A. Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, V.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, V.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.

(16) The comparison between the two types of error calculations gives a measure of the type of reproducibility of the experimental results. Thus, the two extreme cases are (a) the average sum is zero and the average error is large, and (b) the two are equal. Case (a) suggests an alternating effect of reproducibility (i.e., some bonds are calculated to be shorter and some are calculated to be longer than they are). Case (b) suggests that all of the bond lengths are slightly different than the experimental values.

Table 1. Calculated Bond Lengths (Å) of Spiro Compounds 11a-d and 13 and of 2,5-Cyclohexadien-1-one (12) at Different Theoretical Levels[a]
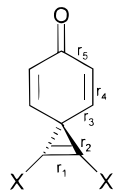
compound	method	r_1	r_2	r_3	r_4	r_5
11a	HF/6-31G*	1.269	1.513	1.484	1.329	1.480
	B3LYP/6-31G*	1.285	1.538	1.478	1.347	1.478
	MP2/6-31G*	1.295	1.532	1.471	1.352	1.473
11b	HF/6-31G*	1.279	1.514	1.484	1.328	1.479
	B3LYP/6-31G*	1.303	1.541	1.477	1.348	1.477
	MP2/6-31G*	1.310	1.536	1.468	1.353	1.472
11c	B3LYP/6-31G*	1.284	1.542	1.486	1.346	1.479
11d	B3LYP/6-31G*	1.289	1.535	1.485	1.343	1.482
4[2c]	B3LYP/6-31G*	1.274	1.632	1.425	1.386	1.404
12	B3LYP/6-31G*			1.499	1.342	1.481
13	B3LYP/6-31G*	1.258	1.610	1.433	1.382	1.406
3		1.297	1.545	1.460	1.349	1.491

[a] The experimental values for **3** are included for comparison.

Table 2. Survey of Average Differences in Bond Lengths (Å) between Structure 3 (Experimental) and 11a and 11b (Calculated)[16]

compound	method	av error in bond-length sum	av error
11a	HF/6-31G*	−0.0111	0.0227
	B3LYP/6-31G*	−0.0027	0.0103
	MP2/6-31G*	−0.0036	0.0102
11b	HF/6-31G*	−0.0099	0.0216
	B3LYP/6-31G*	-4.4×10^{-5}	0.0088
	MP2/6-31G*	−0.0013	0.0104

Table 3. Bond Lengths (Å) of Cyclopropenes 7 and 14 and of the Cyclopropenylic Moiety of 11 at B3LYP/6-31G*

	compound			
	7, 14		**11**	
X/bond	r_1	r_2	r_1	r_2
H	1.295	1.509	1.285	1.538
$H_2C=CH$	1.315	1.507	1.303	1.541
OH	1.291	1.512	1.284	1.542
NO_2	1.293	1.509	1.289	1.535

former giving somewhat lower differences, i.e., better results. Hence, the analysis below is in terms of B3LYP/6-31G*.

The calculated bond lengths of the cyclohexadienone moiety in **11** do not change much on substitution, and they do not differ much from those in **12**. Not suprisingly, these bond lengths differ significantly from those of the bridging phenyl ring in the vinyl cation **13**. The calculated bond lengths of the corresponding 1,2-disubstituted cyclopropene moieties of **11** are somewhat more sensitive to substitution and differ somewhat more (especially r_2) than the calculated bond lengths of the corresponding cyclopropenes **14**, as shown by comparing Tables 1 and 3. The values differ strongly from those for the cyclopropenyl moieties in cations **4** and **13**.

To better understand and to quantify these observations we applied the natural resonance theory (NRT) analysis.[17] This analysis converts the MO density matrix into a resonance picture of the studied system, thus allowing quantification of arguments such as the one presented in Scheme 1. Figures 3 and 4 show the

resonance picture for the spiro compounds **11a−c** and for **7** and **12−14**, respectively. The similarity in the geometries of the cyclohexadienone moieties can be rationalized by the fact that similar structures contribute similarly in **11a−c** and in **12**. Thus, the percentage of contribution of the charged structures of **12** closely resembles those for all of the derivatives of **11**. Generally, the same also applies for the cyclopropenylic fragment of **11** vs the respective isolated cyclopropene moieties **7** and **14**, except that structures with one broken cyclopropenylic bond contribute a little more in **11**, making its r_2 ca. 0.03 Å longer than r_2 in **7** and **14**.

The question of how good a model **3** is for **4** is answered by comparing the data in Table 1 for **4** (calculated, B3LYP/6-31G*)[2c] and **3** (X-ray). The differences are significant: r_1, r_3, and r_5 are 0.023, 0.035, and 0.087 Å longer, and r_2 and r_4 are 0.087 and 0.037 Å shorter, respectively, for **3** than for **4**. The differences between the HF/3-21G calculated values for **4** (see below) and those measured for **3** are even larger. Consequently, the neutral **3** is not a good model for the charged **4**.

Because of the charge difference between **3** and **4**, calculation of a model closer to **4** than **3** is desirable. We have calculated the protonated spiro compound **15** and applied NRT analysis to its structure (Figure 5). Although the symmetry of **15** is C_1, it is clear that its geometrical parameters are in the range between those of **3** and **13**. The NRT analysis shows a similar picture; structures that delocalize the charge on the six-membered ring comprise 39% of **15**, 50% of **13**, and <13% of **11a−c**. In the main contributing structure of **15** that comprises 24% of the structure, the charge is localized on the oxygen, whereas in **11a−c**, the respective non-charged structures contribute 28−53%. Thus, as expected, **15** seems a much better model for **13** (or **1** or **4**) than **3** is. Unfortunately, the oxygen-protonated product of **3** cannot be prepared because protonation of **3** leads to a ring-opening reaction.[4c]

Three-membered rings are known to have curved ("banana") bonds,[20] and it is interesting whether this is also true when the three-membered ring is a part of a spiro junction. In **11** and **12**, the geometries of the six-membered ring are similar, but there is a very large difference in the angle at the spiro junction. The HCH angle in **12** is 103.8°, whereas the respective spiro C(cyclopropyl)CC(cyclopropyl) angles in **11a−c** are 49−50°. To assess the curvature of the cyclopropylic bonds, we optimized **12** with the HC(4)H angle fixed to values between 100° and 50° and calculated the corresponding geometries of the rest of the molecule.[18] The results are summarized in Table 4. The reduction of the HCH angle is accompanied by hybridization changes. The hybrids of the CH bond have more p character and therefore

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(18) This approach was successfully employed in strained aromatic systems. (a) Stanger, A. *J. Am. Chem. Soc.* **1991**, *113*, 8277. (b) Stanger, A. *J. Am. Chem. Soc.* **1998**, *120*, 12034.

(19) (a) Ermer, O.; Lex, J. *Angew. Chem.* **1987**, *99*, 455; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 447. (b) Ermer, O.; Bell, P.; Schäfer, J.; Szeimies, G. *Angew. Chem.* **1989**, *101*, 503; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 473.

(20) See, for example: Streitwieser, A.; Heathcock, C. H.; Kosower, E. M. *Introduction to Organic Chemistry*, 4th ed.; Macmillan Publishing Company: New York, 1992; pp 89−90.
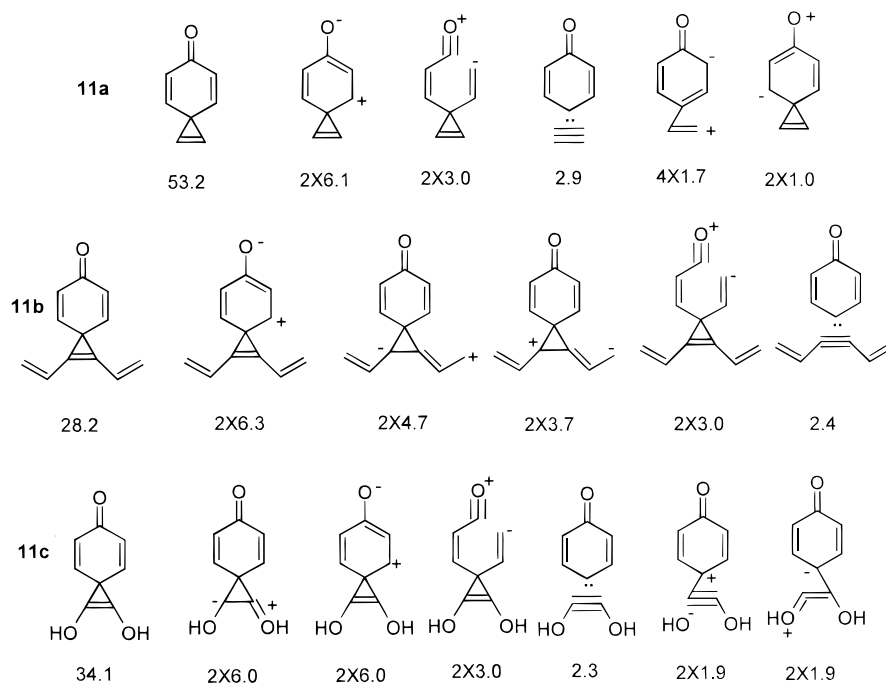
Figure 3. NRT analysis of the spiro derivatives **11a**–**c**. The numbers below the resonance structures represent the percentage contribution to the total structure.
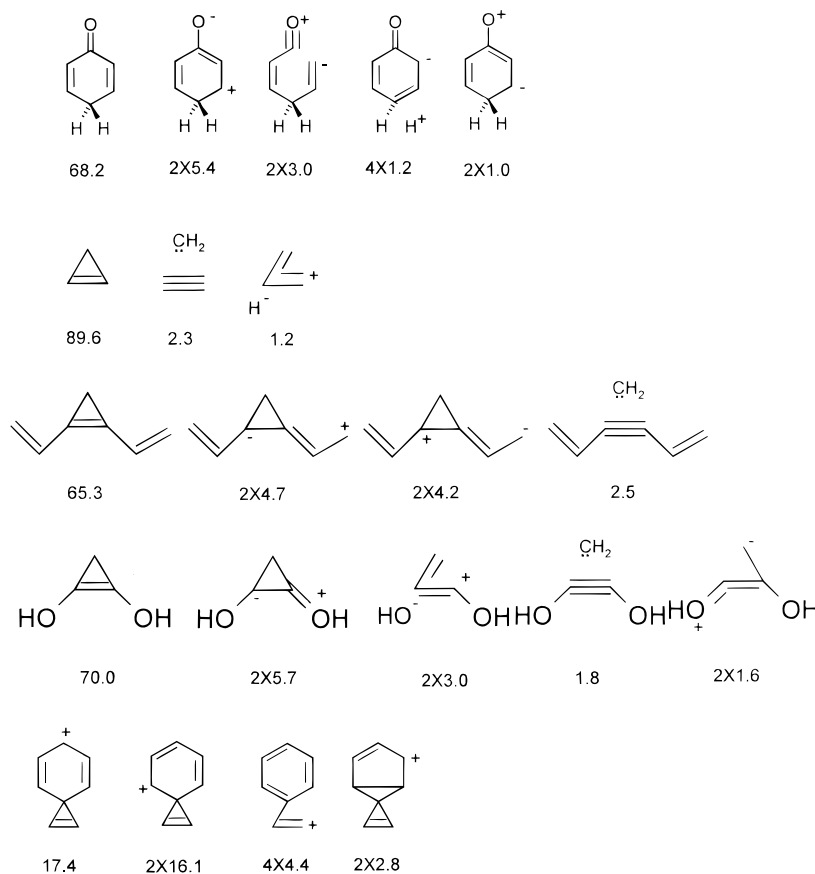

Figure 4. NRT analysis of cyclohexa-2,5-dien-1-one **12** (top), cyclopropenes **7**, **14a**, and **14b** (middle), and vinylidenephenonium ion **13** (bottom). The numbers below the resonance structures represent the percentage contribution to the total structure.

should lengthen, whereas in the remaining hybrids, the s character increases and the CC bonds shorten.[19] From a plot of Δr_3 and ΔC–H bond distance (i.e., the difference between the values of these parameters for a specific HCH angle and the optimized values) as a function of

the HCH angle (Figure 6) it is seen that this is indeed the case. On the basis of the r_3 and r_4 bond lengths in **11**, the spiro angle should be 70–80° and 60–70° (Table 4 and Figure 6), respectively, assuming that the carbon substituents influence only little the r_3 and r_4 bond
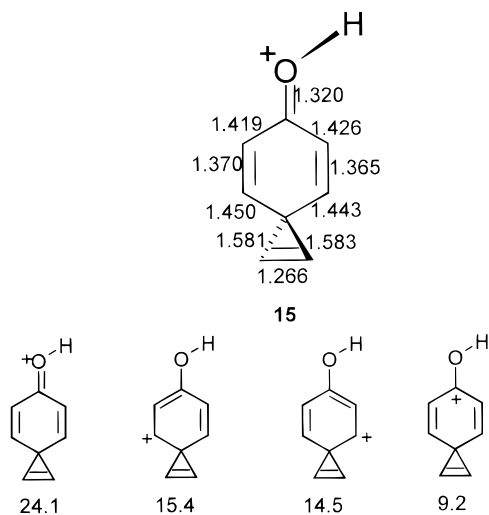
Figure 5. Bond lengths (Å) and NRT analysis (only in structures that delocalize charge on the six-membered ring) of **15**. The numbers below the resonance structures represent the percentage contribution to the total structure.

Table 4. Bond Lengths (Å) of 12 as a Function of the HC(4)H Angle[a]

HC$_4$H	r_3	r_4	r_5	C−H
103.8	1.499	1.342	1.481	1.103
100.0	1.496	1.342	1.481	1.105
90.0	1.488	1.343	1.481	1.110
80.0	1.480	1.344	1.481	1.117
70.0	1.471	1.345	1.480	1.127
60.0	1.460	1.348	1.479	1.140
50.0	1.448	1.351	1.478	1.162
spiro	1.478	1.347	1.478	

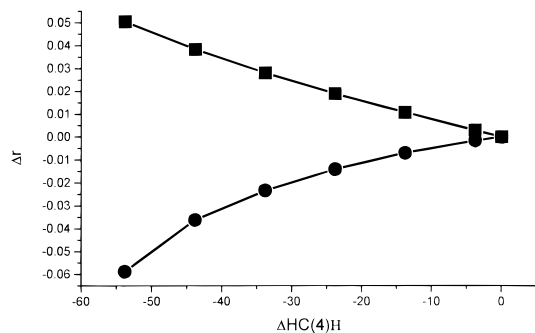[a] The definition of the different parameters is the same as in Table 1.

Figure 6. ΔC−H (■) and Δr_3 (●) as a function of ΔHC(4)H angle (relative to the optimized system).

lengths. Because the observed angle is ca. 50°, we conclude that the cyclopropenylic bonds in the spiro fusion are curved.

This conclusion may be relevant to the difference between the X-ray structure of **3** and the recent HF/3-21G calculations[2b] on **4** which gave the following parameters for the cyclopropenyl moiety: C(1)C(3)−C(2) 44.2°, C=C 1.251 Å, =C−C 1.663 Å, C−Ph 1.438 Å. For a substituted ion **4**, when the bridging phenyl is replaced

by a bridging mesityl, the results show C(1)C(3)−C(2) 46.0°, C=C 1.260 Å, C−C 1.611 Å, C−Ph 1.439 Å. These values reflect mainly the different effect of feature (c) on the two structures. It will be of interest to study less symmetrical analogues of **3** at C(1) and C(2) in order to compare their parameters with predictions concerning the structures of the corresponding nonsymmetrical vinylidenephenonium ions.

Conclusions

The following conclusions are drawn from our data: (a) The C(1)C(3)C(2) spiro angle in **3** (49.64(7)°) is one of the smallest known for an sp^3 hybridized carbon atom. Yet, it does not affect the "normal" relation between the C=O bond length and the difference between the single and double bond lengths in the cyclohexadienone moiety. (b) Both structural criteria and NRT analyses suggest that the neutral **3** is not a good model for the charged bridged vinylidenephenonium ion **4**. The charged O-protonated spirotrienone **15** is calculated to be a much better model for **4**. (c) The single bonds in the cyclopropenyl moiety are curved, leading to an effective calculated spiro bond angle of ca. 70°, whereas the respective measured bond angle in **3** is < 50°.

Experimental Section

The X-ray structure of **3** as shown in Figure 1 ($C_{28}H_{30}O$, MG 382.52) was determined from a yellow, plate-shaped crystal with the approximate size 0.32 × 0.24 × 0.07 mm^3 at 120 K on a Nicolet R3 diffractometer with graphite-monochromatized Mo Kα radiation. The cell dimensions of the monoclinic system were determined from 50 centered reflections in the 2Θ-range 20−25°: a = 16.443(3), b = 10.441(2), c = 13.556(2) Å, β = 94.670(13)°, V = 2319.6(7) Å^3, space group $I2$/a, F_{ooo} = 824, μ = 0.064 mm^{-1}, ρ_{calc} = 1.095 g cm^{-3}, 7236 collected intensities (2Θ$_{max}$ = 70°, 0 ≤ h ≤ 26; −12 ≤ k ≤ 16; −21 ≤ l ≤ 21), 5103 independent (R_{merg} = 0.0397), 3570 observed [I > 2σ(I)], structure solution with direct methods and refinement on F^2 with Siemens SHELXTL-program package Vers. 5.03, 142 parameters (hydrogen atoms as riding groups, groupwise isotropical U-values), GooF = 1.020, w^{-1} = $\sigma^2(F_o{}^2)$ + (0.0654P)^2 + 0.47P, where P = [(max$F_o{}^2$) + (2$F_c{}^2$)]/3, no extinction correction, R1 (obs data) = 0.0481, wR2 (all data) = 0.1390, maximum shift < 0.001, residual electron density 0.462 e Å^{-3} between C(2) and C(2′). A structure refinement with 1516 intensities and 1277 observed data (restricted to 2Θ$_{max}$ = 45°) produced much better R-values: R1 (obs data) = 0.0322, wR2 (all data) = 0.0882. Further details of the crystal structure investigation are available on request from the CCDC.

Supporting Information Available: Geometries of **11**−**13** (Table S1), of cyclopropene derivatives (**7** and **14**) (Table S2), of **15** (Figure S1) at HF/6-31G*, B3LYP/6-31G*, and MP2/6-31G* (Table S1), and the full NRT analysis of **15** (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.