PERKIN 2

Extended conjugation in enynones, dienones and related species: a theoretical and experimental study. The molecular structures of 3-ethynyl-2-methylcyclopent-2-enone, 3-ethenyl-2-methylcyclopent-2-enone and 3-ethyl-2-methylcyclopent-2-enone, as studied by gas electron diffraction

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The molecular structures of three 3-R substituted conjugated enones have been determined by the gas electron diffraction method. Depending on the nature of the substituents the molecules represent examples of molecules with no additional conjugation, relative to that of the enone system (R = CH_3CH_2-), or those with extended conjugation involving different π systems (R = CH_2=CH-; R = HC≡C-). The molecular structures of the three enones have also been calculated by *ab initio* MP2/6-31G* optimizations.

In order to better understand the conjugative effects of ethenyl and ethynyl substituents on a conjugated enone system, a large number of hydrogenation reactions and substituent exchange reactions have been studied, based on the energies of the various molecules involved in the reactions, as calculated by MP2/6-31G* optimizations. The studies indicate that the conjugative effect of an ethenyl substituent on a conjugated enone system is approximately 4.2 kcal mol^{-1}, while that of an ethynyl substituent is considerably lower and more variable; on average *ca.* 2.3 kcal mol^{-1}.

Introduction

Despite considerable interest in the chemistry of enones,[1] *i.e.* α,β-unsaturated carbonyl compounds, surprisingly little is known about the systematics of their structures[2] and their energetics.[3] Far less is known about derivatives with more extended conjugation, either with an appended C≡C triple bond or a second C=C double bond. The intention of the present paper is to contribute to the knowledge within this field.

The molecular structures of three similar β-substituted, conjugated enones, that differ from one another only in the potential of the β-substituent to (if unsaturated) conjugate with the π electrons of the enone system, have been studied by the gas electron diffraction (GED) method. The three molecules are: 3-ethynyl-2-methylcyclopent-2-enone (ENONYN), 3-ethenyl-2-methylcyclopent-2-enone (ENONEN) and 3-ethyl-2-methylcyclopent-2-enone (ENONET). The β-substituent of each compound corresponds to an HC≡C-, an H_2C=CH- and a H_3CCH_2-group, respectively. Barring sufficient quantity of material for measurement by bomb (oxygen) calorimetry and insufficient stability or excessive catalytic affinity for hydrogenation calorimetry, experimental determination of enthalpies of formation and of the energetics of these molecules is futile. *Ab initio* (MP2/6-31G*//MP2/6-31G*) quantum chemical calculations on these, as well as on a series of structurally related model compounds, have therefore been performed in the hope of better understanding the energetics of these molecules.

Experimental

Syntheses: general techniques

^{1}H NMR spectra were obtained using Varian T-60, IBM NR-80, Varian Inova 300, or General Electric GN-500 spectrometers operating at 60, 80, 300 and 500 MHz, respectively. ^{13}C NMR spectra were obtained using a Varian Inova 300 spectrometer operating at 75 MHz. IR spectra were obtained using a Perkin-Elmer 1420 spectrophotometer. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA. Flash chromatography[4] was performed using 200–425 mesh Fisher silica gel. Preparative gas chromatography was performed on a Gow-Mac 580 instrument using a 6″ × $\frac{1}{4}$″ 10% DC-550 column at 140 °C. THF and diethyl ether were distilled from sodium–benzophenone. Light petroleum (Fisher) was used as received. Acetylene gas was purified before use by passage through a series of traps consisting of a −78 °C trap, concentrated H_2SO_4, safety trap and KOH. Butyllithium, ethenylmagnesium bromide and ethylmagnesium bromide (Aldrich) were titrated before use.

Syntheses: preparation of compounds

All compounds were stored as 1.0 g samples sealed in glass ampoules under argon. 3-Ethynyl-2-methylcyclopent-2-enone[6] was prepared from 3-isobutoxy-2-methylcyclopent-2-enone.[7]

3-Ethenyl-2-methylcyclopent-2-enone. An oven-dried, argon-purged 250 cm^3 round-bottom flask equipped with magnetic stirring bar, constant pressure addition funnel and argon inlet adapter was charged with 49 cm^3 of a 1.07 mol dm^{-3} THF solution of ethenylmagnesium bromide, followed by 37 cm^3 of THF. The flask was cooled to −78 °C using a dry ice–acetone bath. A solution of 3-isobutoxy-2-methylcyclopent-2-enone (4.54 g, 27.0 mmol) in 25 cm^3 of THF was added at a rate of 2–5 drops per minute. Once the addition was complete, the dry ice–acetone bath was removed and the reaction left to stir as it warmed to room temperature. Once it reached that tempera-

Table 1 Experimental conditions for the gas electron diffraction experiments carried out on the three 3-substituted cyclopent-2-enone molecules

	ENONYN	ENONEN	ENONET
Long camera data:			
Temperature/°C	76	36	26
Wavelength/Å	0.058 700	0.058 720	0.058 700
No. of plates[a]	4	6	3
Nozzle-to plate distance/mm:	498.72	498.46	498.72
Data range:			
s_{min}/Å^{-1}	1.25	1.75	1.50
s_{max}/Å^{-1}	15.50	15.50	15.25
Δs/Å^{-1}	0.25	0.25	0.25
Short camera data:			
Temperature/°C	60	39	35
Wavelength/Å	0.058 700	0.058 720	0.058 700
No. of plates[a]	4	6	4
Nozzle-to plate distance/mm:	248.86	248.77	249.09
s_{min}/Å^{-1}	2.75	3.50	3.00
s_{max}/Å^{-1}	30.25	30.25	30.25
Δs/Å^{-1}	0.25	0.25	0.25

[a] Kodak Electron Image photographic plates.

Table 2 Molecular structure parameters for the three 3-substituted cyclopent-2-enones, as obtained from *ab initio* MP2/6-31G* fully optimized calculations

	ENONYN	ENONEN	ENONET
$r(C^2{=}C^3)$	1.3590	1.3611	1.3545
$r(C{=}O)$	1.2286	1.2294	1.2289
$r(C^1{-}C^2)$	1.4786	1.4770	1.4780
$r(C^3{-}C^4)$	1.5177	1.5171	1.5148
$r(C^4{-}C^5)$	1.5348	1.5341	1.5337
$r(C^1{-}C^5)$	1.5279	1.5256	1.5272
$r(C^2{-}C^8)$	1.4891	1.4920	1.4928
$r(C^3{-}C^6)$	1.4199	1.4535	1.4966
$r(C^6{-}C^7)$	1.2246	1.3469	1.5348
$\angle C^5{-}C^1{-}C^2$	108.44	108.40	108.35
$\angle C^1{-}C^2{-}C^3$	108.94	109.58	109.55
$\angle C^2{-}C^3{-}C^4$	113.11	112.09	112.33
$\angle C^3{-}C^4{-}C^5$	104.20	104.97	104.99
$\angle C^4{-}C^5{-}C^1$	105.31	104.96	104.77
$\angle C^2{-}C^1{=}O$	125.48	125.56	125.73
$\angle C^3{=}C^2{-}CH_3$	129.26	130.64	130.38
$\angle C^2{=}C^3{-}C^6$	125.42	126.04	127.40
$\angle C^3{-}C^6{-}C^7$	180.00	123.93	111.78
$\varphi(C^2{=}C^3{-}C^6{-}C^7)$	—	180.00	98.42
E (Hartree/molecule)	−383.590 453 3	−384.805 665 4	−386.004 236

Table 3 Energies (in Hartrees/molecule) for molecules of interest relative to the energetics of conjugated enones, as obtained from *ab initio* MP2/6-31G*//MP2/6-31G* calculations

No.	Molecule	Energy
1	H_2	−1.144 141
2	$CH_3{-}CH_3$	−79.494 741
3	$CH_3{-}C{\equiv}CH$	−116.241 812
4	$CH_3{-}CH_2{=}CH_2$	−117.455 545
5	$CH_3{-}CH_2{-}CH_3$	−118.660 343
6	$CH_2{=}CH{-}C{\equiv}CH$	−154.205 626
7	$CH_2{=}CH{-}CH{=}CH_2$	−155.422 655
8	$CH{\equiv}C{-}CH_2{-}CH_3$	−155.407 440
9	$CH_2{=}CH{-}CH_2{-}CH_3$	−156.621 194
10	(Z)-$CH_3{-}CH{=}CH{-}CH_3$	−156.623 473
11	(E)-$CH_3{-}CH{=}CH{-}CH_3$	−156.625 924
12	$CH_3{-}CH_2{-}CH_2{-}CH_3$	−157.826 037
13	(E)-$CH_3{-}CH{=}CH{-}C{\equiv}CH$	−193.377 563
14	(Z)-$CH_3{-}CH{=}CH{-}C{\equiv}CH$	−193.377 813
15	$CH{\equiv}C{-}CH_2{-}CH_2{-}CH_3$ (*anti*)	−194.573 427
16	$CH{\equiv}C{-}CH_2{-}CH_2{-}CH_3$ (*gauche*)	−194.573 983
17	(Z)-$CH_3{-}CH{=}CH{-}CH{=}CH_2$	−194.591 366
18	(E)-$CH_3{-}CH{=}CH{-}CH{=}CH_2$	−194.593 851
19	$CH_2{=}CH{-}CH_2{-}CH_2{-}CH_3$	−195.787 116
20	(Z)-$CH_3{-}CH{=}CH{-}CH_2{-}CH_3$	−195.789 192
21	(E)-$CH_3{-}CH{=}CH{-}CH_2{-}CH_3$	−195.791 737
22	$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_3$	−196.991 726
23	(Z)-$O{=}CH{-}CH{=}CH{-}CH_3$	−230.479 684
24	(E)-$O{=}CH{-}CH{=}CH{-}CH_3$	−230.484 292
25	$O{=}CH{-}C(CH_3){=}CH_2$	−230.485 404
26	(Z)-$O{=}CH{-}CH{=}CH{-}C{\equiv}CH$	−267.231 404
27	(E)-$O{=}CH{-}CH{=}CH{-}C{\equiv}CH$	−267.232 804
28	$O{=}CH{-}CH_2{-}CH_2{-}C{\equiv}CH$	−268.421 929
29	(Z)-$O{=}CH{-}CH{=}CH{-}CH{=}CH_2$	−268.447 108
30	(E)-$O{=}CH{-}CH{=}CH{-}CH{=}CH_2$	−268.451 720
31	(Z)-$O{=}CH{-}CH{=}CH{-}CH_2{-}CH_3$	−269.645 496
32	(E)-$O{=}CH{-}CH{=}CH{-}CH_2{-}CH_3$	−269.650 051
33	$O{=}CH{-}C(CH_3){=}CH{-}CH_3$	−269.656 121
34	$O{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$	
35	$O{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH_3$	−270.842 010
36	(E)-$O{=}CH{-}C(CH_3){=}CH{-}C{\equiv}CH$	−306.408 430
37	(E)-$O{=}CH{-}C(CH_3){=}CH{-}CH{=}CH_2$	−307.624 311
38	(E)-$O{=}CH{-}C(CH_3){=}CH{-}CH_2{-}CH_3$	−308.821 957
39	2,3-Dimethylcyclopent-2-enone	−346.838 823
40	ENONYN	−383.590 453
41	ENONEN	−384.805 665
42	ENONET	−386.004 236

ture, it was left to stir for an additional hour. 10 cm^3 of water was added, followed by addition of 1 g K_2CO_3. The contents of the flasks were transferred to a separatory funnel, 200 cm^3 of ether was added, then the whole was washed well with 100 cm^3 of water. The aqueous layer was back-extracted once with 50 cm^3 of ether. The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated by rotary evaporation to provide a liquid which was transferred to a 125 cm^3 Ehrlenmeyer flask with 25 cm^3 of diethyl ether. 10 cm^3 of 1 mol dm^{-3} HCl was added and the mixture stirred rapidly for 2 h. The contents of the flask then were transferred to a separating funnel using 20 cm^3 of ether and the aqueous layer was removed. The organic layer was washed sequentially with saturated aqueous $NaHCO_3$, water and brine. Drying ($MgSO_4$) was followed by filtration and concentration by rotary evaporation to give the crude product as a liquid.

Flash chromatography (4 : 1 light petroleum–ether) gave 1.70 g (49%) of 3-ethenyl-2-methylcyclopent-2-enone: bp 38 °C (0.3 mmHg) (lit.,[8] bp 63 °C at 1.5 mmHg). IR (ν/cm^{-1}) (thin film): 3360 (w), 3090 (w), 3010 (w), 2950 (m), 2920 (s), 2860 (w), 2840 (w), 1900 (w), 1690 (s), 1635 (s), 1585 (s), 1440 (m), 1425 (m), 1410 (m), 1380 (m), 1040 (m), 990 (m), 930 (m), 835 (m), 825 (m). ^{1}H NMR ($CDCl_3$): d 7.34 (d, $J = 5$ Hz, 1H), 7.05 (d, $J = 5$ Hz, 1H), 6.0 (d, $J = 8$ Hz, 2H), 5.6 (d, $J = 5$ Hz, 2H), 2.6–3.1 (m, 4H), 2.1 (t, $J = 1$ Hz, 3H).

3-Ethyl-2-methylcyclopent-2-enone. The crude product was prepared and isolated in a manner analogous to the preparation of 3-ethenyl-2-methylcyclopent-2-enone. Thus, 37 cm^3 of a 1.18 mol dm^{-3} solution of ethylmagnesium bromide in THF and 4.54 g (27 mmol) of 3-isobutoxy-2-methylcyclopent-2-enone provided a crude product which was purified by flash chromatography (4 : 1 light petroleum–ether) to give 2.0 g (59%) of 3-ethyl-2-methylcyclopent-2-enone: bp 24–25 °C (0.05 mmHg). IR (ν/cm^{-1}) (thin film): 2960 (m), 2910 (m), 2860 (w), 1695 (s), 1640 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): d 2.57 (m, 2H), 2.50 (d, $J = 6.7$ Hz, 2H), 2.38 (m, 2H), 2.68 (s, 3H), 1.15 (t, $J = 6.7$ Hz). ^{13}C NMR ($CDCl_3$): d 210.2, 174.9, 135.7, 34.3, 28.8, 19.3, 11.7, 7.9. Analytical samples prepared either by Kugelrohr distillation or by preparative gas chromatography provided the ketone as a trimolecular hydrate: Elemental analysis: calculated for $(C_8H_{12}O)_3{\cdot}H_2O$, C, 73.79; H, 9.31. Found C, 73.79; H, 9.35%.

Gas electron diffraction recordings

Electron diffraction diagrams of the three enones were recorded with a Balzer's Eldigraph KD-G2 unit,[9,10] using an r^3-sector and Kodak electron image plates. The scattered electrons were recorded at nominal nozzle-to-plate distances of 500 mm (long camera, LC) and 250 mm (short camera, SC). The experimental

Table 4 Vibrational amplitudes for the C–C and C–O distances in the three 3-substituted cyclopent-2-enones, as calculated by ASYM40[13] and based on *ab initio* MP2/6-31G* force fields[a,b]

		ENONYN	ENONEN	ENONET
$C^2{=}C^3$		0.0411	0.0412	0.0411
$C{=}O$		0.0362	0.0360	0.0363
$C^1{-}C^2$		0.0493	0.0489	0.0488
$C^3{-}C^4$		0.0506	0.0501	0.0504
$C^4{-}C^5$		0.0509	0.0505	0.0505
$C^1{-}C^5$		0.0509	0.0502	0.0505
$C^2{-}CH_3$		0.0490	0.0487	0.0488
$C^3{-}C^6$		0.0456	0.0475	0.0495
$C^6{-}C^7$		0.0349	0.0407	0.0513
$C^2{\cdot}O$		0.0578	0.0579	0.0564
$C^5{\cdot}O$		0.0600	0.0591	0.0587
$C^8{\cdot}{\cdot}O$		0.1067	0.0998	0.1000
$C^3{\cdot}{\cdot}O$		0.0546	0.0577	0.0536
$C^4{\cdot}{\cdot}O$		0.0579	0.0597	0.0568
$C^6{\cdots}O$		0.0652	0.0699	0.0658
$C^7{\cdots}O$	$\longrightarrow$	0.0805	0.0774	0.1866
$C^1{\cdot}C^3$		0.0531	0.0542	0.0523
$C^2{\cdot}C^4$		0.0545	0.0538	0.0539
$C^3{\cdot}C^5$		0.0574	0.0577	0.0569
$C^1{\cdot}C^4$		0.0561	0.0561	0.0552
$C^2{\cdot}C^5$		0.0566	0.0558	0.0588
$C^2{\cdot}C^6$		0.0613	0.0607	0.0613
$C^4{\cdot}C^6$		0.0703	0.0688	0.0568
$C^3{\cdot}C^8$		0.0630	0.0617	0.0612
$C^1{\cdot}C^8$		0.0715	0.0697	0.0685
$C^3{\cdot}C^7$		0.0493	0.0609	0.0753
$C^6{\cdot}{\cdot}C^8$		0.1070	0.0932	0.0963
$C^2{\cdot}{\cdot}C^7$	$\longrightarrow$	0.0831	0.0626	0.1758
$C^4{\cdot}{\cdot}C^7$	$\longrightarrow$	0.0972	0.1063	0.1825
$C^1{\cdot}{\cdot}C^6$		0.0602	0.0647	0.0619
$C^5{\cdot}{\cdot}C^6$		0.0647	0.0675	0.0659
$C^4{\cdot}{\cdot}C^8$		0.0642	0.0644	0.0630
$C^5{\cdot}{\cdot}C^8$		0.0673	0.0692	0.0657
$C^7{\cdots}C^8$	$\longrightarrow$	0.1635	0.0945	0.3111
$C^1{\cdots}C^7$	$\longrightarrow$	0.0670	0.0780	0.1463
$C^5{\cdots}C^7$	$\longrightarrow$	0.0746	0.1003	0.1411

[a] The vibrational amplitudes that are very different in the three molecules are marked by an arrow. [b] The number of bond angles between two atoms are illustrated by dots.

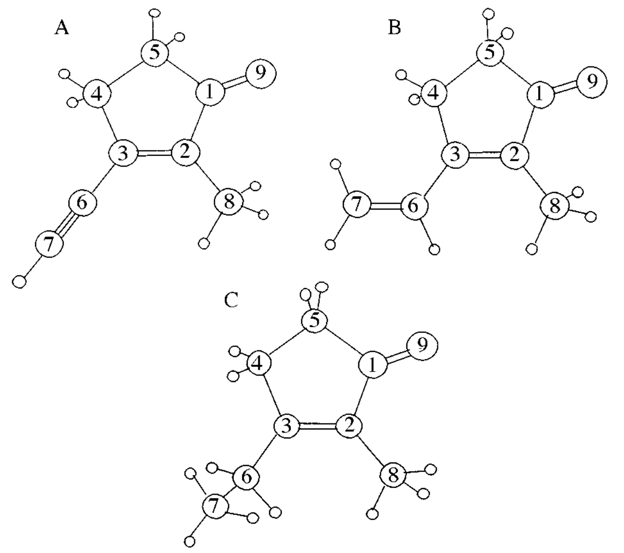

Fig. 1 Molecular models for (A) 3-ethynyl-2-methylcyclopent-2-enone, (B) 3-ethenyl-2-methylcyclopent-2-enone and (C) 3-ethyl-2-methylcyclopent-2-enone, showing the numbering of the atoms as they are referred to in the paper

details of the two sets of exposures for each of the three molecules, are summarised in Table 1.

Ab initio calculations

The computations were performed using the GAUSSIAN94 program package.[11] In the introductory stage of the study HF/6-31G* optimisations were calculated. The results that are reported here are, however, exclusively based on MP2/6-31G* optimisations, which have been carried out for the three cyclopentenone derivatives, whose structures have been studied experimentally, as well as for a number of structurally related molecules.

Table 2 shows the structure parameters obtained for the three 3-substituted-2-methylcyclopentenones from fully optimised *ab initio* MP2/6-31G* calculations. The ENONYN molecule has no conformational freedom, while other conformers than those presented in Table 2 should in principle be considered for ENONEN and ENONET. HF/6-31G* optimisations were attempted for the s-*trans* and s-*syn* conformers of ENONEN. The calculation for the s-*syn* conformer did, however, converge towards the s-*trans* form. MM3 calculations[12] of the ENONEN potential energy for rotation around the C^3–C^6 bond, gave minima at ±30° and at 180°, the former being destabilised by 3.5 kcal mol^{-1} relative to the s-*anti* conformer. For ENONET *ab initio* HF/6-31G* optimisations of the *syn* and *skew* conformers gave an energy difference between the two of 4.1 kcal mol^{-1} in favour of the *skew* conformer.

Table 3 presents the calculated energies (in Hartrees/molecule) for a series of molecules that are structurally related to the three cyclopentenones. The data will be referred to in the discussion below. For one molecule, 4-pentenal (Table 3, entry 34), the optimisation calculations resulted in oscillating energies, and it was not possible to obtain an energy minimum. The alternative solution of constructing an average or idealised geometry with associated energy was decided against, as the 4-pentenal energy was intended to be used for calculating the conjugative effect of a vinyl group, and calculations based on nine other reactions gave nearly identical results for this effect.

Frequency calculations, based on the fully optimised *ab initio* MP2/6-31G* structures, were also carried out for the three substituted cyclopent-2-enones, and the generated force fields were used to calculate the vibrational amplitudes for the molecules (see below and Table 4).

Gas electron diffraction studies

The molecular structures of 3-ethynyl-2-methylcyclopent-2-enone, 3-ethenyl-2-methylcyclopent-2-enone and 3-ethyl-2-methylcyclopent-2-enone have been determined from least-squares refinements of the molecular intensity data for each of them, combined with information obtained from the *ab initio* calculations, see Table 2. Vibrational amplitudes (u_{ij}) and perpendicular correction coefficients (K_{ij}) for all interatomic distances were calculated by the program ASYM40.[13] The Cartesian force constants calculated by the GAUSSIAN94 program at the MP2/6-31G* level were used as initial force fields. Since frequencies computed at the HF or MP2 level are generally overestimated by 10–20%, scaling factors equal to 0.900 were applied.[12] The vibrational amplitudes (see Table 4) and shrinkage corrections for the three cyclopentenone derivatives were calculated from the scaled force fields. The geometries of the molecules were based on r_a molecular models, which include corrections for shrinkage effects.[14]

Molecular models for the three cyclopent-2-enones, including numbering of the heavy atoms, are shown in Fig. 1. For the sake of simplicity, when comparing the three structures, the same atom numbering system has been used for all the molecules.

None of the three cyclopent-2-enone derivatives that have been studied by GED have any symmetry, and a large number of geometrical parameters are required in order to describe their molecular models. Each of the eight C–C distances in one of these molecules is for example in principle unique, but many

Table 5 CC/CO distance constraints applied in the restricted GED models (see Table 6). The constraints are based on results from the MP2 calculations (see Table 2)

	$\Delta\mathrm{MP2} = \Delta r_{\mathbf{a}}/\text{Å}$	$\Delta r_{\alpha}/\text{Å}$
ENONYN		
1. $r(\mathrm{C{=}O}) - r(\mathrm{C{\equiv}C})$	0.0040	0.0063
2. $r(\mathrm{C^2{-}C^8}) - r(\mathrm{C^1{-}C^2})$	0.0105	0.0086
3. $r(\mathrm{C^1{-}C^5}) - r(\mathrm{C^3{-}C^4})$	0.0102	0.0053
4. $r(\mathrm{C^4{-}C^5}) - r(\mathrm{C^3{-}C^4})$	0.0171	0.0012
ENONEN		
1. $r(\mathrm{C^2{=}C^3}) - r(\mathrm{C^6{=}C^7})$	0.0142	0.0294
2. $r(\mathrm{C^1{-}C^2}) - r(\mathrm{C^3{-}C^6})$	0.0235	0.0284
3. $r(\mathrm{C^2{-}C^8}) - r(\mathrm{C^3{-}C^6})$	0.0385	0.0382
4. $r(\mathrm{C^1{-}C^5}) - r(\mathrm{C^3{-}C^4})$	0.0085	0.0040
5. $r(\mathrm{C^4{-}C^5}) - r(\mathrm{C^3{-}C^4})$	0.0170	0.0092
ENONET		
1. $r(\mathrm{C^3{-}C^6}) - r(\mathrm{C^2{-}C^8})$	0.0038	0.0068
2. $r(\mathrm{C^1{-}C^5}) - r(\mathrm{C^3{-}C^4})$	0.0124	0.0081
3. $r(\mathrm{C^4{-}C^5}) - r(\mathrm{C^3{-}C^4})$	0.0189	0.0014

Table 6 Molecular structure parameters[a] for the three 3-substituted cyclopent-2-enones, as obtained from GED data (restricted model)

	ENONYN	ENONEN	ENONET
$r(\mathrm{C^2{=}C^3})$	1.3771(31)	1.3629(17)	1.3708(24)
$r(\mathrm{C{=}O})$	1.2266(8)	1.2227(19)	1.2395(17)
$r(\mathrm{C^1{-}C^2})$	1.4762(15)	1.4817(11)	1.4748(60)
$r(\mathrm{C^3{-}C^4})$	1.5256(9)	1.5192(10)	1.5302(27)
$r(\mathrm{C^4{-}C^5})$	1.5427(9)	1.5355(10)	1.5273(27)
$r(\mathrm{C^1{-}C^5})$	1.5358(9)	1.5201(10)	1.5331(27)
$r(\mathrm{C^2{-}CH_3})$	1.4867(15)	1.4981(11)	1.4910(18)
$r(\mathrm{C^3{-}C^6})$	1.4169(29)	1.4669(11)	1.4961(18)
$r(\mathrm{C^6{-}C^7})$	1.2226(8)	1.3502(17)	1.5588(87)
$r(\mathrm{C_{sp/sp^2}{-}H})$	1.1081(22)	1.0203(61)	—
$r(\mathrm{C_{sp^3}{-}H})$	1.1130(22)	1.1159(29)	1.1128(15)
$\angle \mathrm{C^5{-}C^1{-}C^2}$	109.46(20)	108.80(28)	108.33(24)
$\angle \mathrm{C^1{-}C^2{-}C^3}$	108.46(16)	108.22(21)	108.97(39)
$\angle \mathrm{C^2{-}C^3{-}C^4}$	112.10(21)	113.21(26)	112.01(31)
$\angle \mathrm{C^3{-}C^4{-}C^5}$	105.34(24)	104.02(29)	104.78(32)
$\angle \mathrm{C^4{-}C^5{-}C^1}$	104.63(23)	105.74(34)	105.91(30)
$\angle \mathrm{C^2{-}C^1{=}O}$	124.11(27)	126.65(95)	124.16(52)
$\angle \mathrm{C^3{=}C^2{-}CH_3}$	130.24(33)	130.64(78)	129.76(55)
$\angle \mathrm{C^2{=}C^3{-}C^6}$	125.72(37)	127.05(46)	126.17(49)
$\angle \mathrm{C^3{-}C^6{-}C^7}$	(180.00)	123.85(51)	111.57(63)
$\varphi(\mathrm{C^2{=}C^3{-}C^6{-}C^7})$	—	180.00	(102.5)
$\mathrm{R^1}$ (L.C.)[b]	0.050 33	0.051 61	0.038 28
$\mathrm{R^2}$ (S.C.)[b]	0.073 02	0.088 09	0.071 05

[a] Distances ($r_{\mathbf{a}}$)/Å and angles ($\angle_{\alpha}$)/°. Standard deviations in parentheses.
[b] $R = [(\Sigma I_{\mathbf{calc}} - I_{\mathbf{obs}})^2/\Sigma(I_{\mathbf{obs}})^2]^{\frac{1}{2}}$.

Table 7 Molecular structure parameters[a] for the three 3-substituted cyclopent-2-enones, as obtained from GED data (unrestricted model)

	ENONYN	ENONEN	ENONET
$r(\mathrm{C^2{=}C^3})$	1.3740(36)	1.3733(38)	1.3681(30)
$r(\mathrm{C{=}O})$	1.2154(22)	1.2221(19)	1.2389(17)
$r(\mathrm{C^1{-}C^2})$	1.4715(53)	1.4789(89)	1.5018(157)
$r(\mathrm{C^3{-}C^4})$	1.5091(88)	1.5190(164)	1.5354(199)
$r(\mathrm{C^4{-}C^5})$	1.5266(87)	1.5264(121)	1.5547(95)
$r(\mathrm{C^1{-}C^5})$	1.5659(59)	1.5272(127)	1.4917(85)
$r(\mathrm{C^2{-}CH_3})$	1.5011(31)	1.5074(69)	1.4896(60)
$r(\mathrm{C^3{-}C^6})$	1.4188(29)	1.4556(76)	1.4882(61)
$r(\mathrm{C^6{-}C^7})$	1.2376(28)	1.3372(46)	1.5496(122)
$r(\mathrm{C_{sp/sp^2}{-}H})$	1.0798(22)	1.021(60)	—
$r(\mathrm{C_{sp^3}{-}H})$	1.1115(22)	1.1127(31)	1.112 3(15)
$\angle \mathrm{C^5{-}C^1{-}C^2}$	108.26(39)	108.49(51)	109.77(29)
$\angle \mathrm{C^1{-}C^2{-}C^3}$	109.03(23)	108.46(36)	107.53(106)
$\angle \mathrm{C^2{-}C^3{-}C^4}$	112.17(29)	112.64(52)	112.74(96)
$\angle \mathrm{C^3{-}C^4{-}C^5}$	106.31(32)	104.46(78)	103.98(37)
$\angle \mathrm{C^4{-}C^5{-}C^1}$	104.22(36)	105.95(70)	105.98(46)
$\angle \mathrm{C^2{-}C^1{=}O}$	125.67(43)	126.53(141)	
$\angle \mathrm{C^3{=}C^2{-}CH_3}$	130.32(47)	129.82(93)	128.59(141)
$\angle \mathrm{C^2{=}C^3{-}C^6}$	125.89(49)	128.30(103)	129.05(172)
$\angle \mathrm{C^3{-}C^6{-}C^7}$	(180.00)	126.92(112)	112.95(68)
$\varphi(\mathrm{C^2{=}C^3{-}C^6{-}C^7})$	—	(180.00)	(102.5)
$\mathrm{R^1}$ (L.C.)[b]	0.047 38	0.049 21	0.039 20
$\mathrm{R^2}$ (L.C.)[b]	0.065 26	0.084 47	0.066 48

[a] Distances ($r_{\mathbf{a}}$)/Å and angles ($\angle_{\alpha}$)/°. Standard deviations in parentheses.
[b] $R = [(\Sigma I_{\mathbf{calc}} - I_{\mathbf{obs}})^2/\Sigma(I_{\mathbf{obs}})^2]^{\frac{1}{2}}$.

of them are expected to be of similar magnitude. It is therefore not possible to determine all of these parameters independently with high precision, and it is necessary to introduce some parameter constraints. These are based on the differences between similar structure parameters, resulting from the *ab initio* MP2/6-31G* optimisations carried out for each of the three molecules. The constraints that have been applied for the CC bonds of the three molecules are presented in Table 5. It is not trivial at which r level the constraints are introduced. This is clearly illustrated by the numbers in Table 5, which show the relationship between bond distance differences based on $r_{\mathbf{a}}$ and r_{α} presentations. As the r_{α} distances are heavily influenced by shrinkage effects, due to perpendicular amplitude vibrations which affect the various bonds differently, it is reasonable to assume that $r_{\mathbf{a}}$ differences will be closest to the $r_{\mathbf{e}}$ differences, as represented by the parameters obtained from *ab initio* calculations. The parameter constraints evaluated from the MP2/6-31G* optimised structures, were accordingly introduced in the $r_{\mathbf{a}}$ structures and were transferred to the r_{α} models, which are the basis for calculating the nonbonded distances in the molecules.

The molecular models of the three cyclopentenone derivatives were described by 21 (ENONYN), 24 (ENONEN) and 22 (ENONET) parameters, respectively, including the bond distances constraints. They were the following:

ENONYN: $r(\mathrm{C{\equiv}C})$, $r(\mathrm{C^2{=}C^3})$, $r(\mathrm{C^3{-}C^6})$, $r(\mathrm{C^1{-}C^2})$, $r(\mathrm{C_{sp^3}{-}H})$, $\Delta[r(\mathrm{C_{sp^3}{-}H}) - r(\mathrm{C_{sp}{-}H})]$, $\angle \mathrm{C^2{-}C^3{-}C^4}$, $\angle \mathrm{C^1{-}C^2{-}C^3}$, $\angle \mathrm{C^2{-}C^1{=}O}$, $\angle \mathrm{C^2{=}C^3{-}C^6}$, $\angle \mathrm{C^3{=}C^2{-}CH_3}$, $\angle \mathrm{C^3{-}C^4{-}H}$, $\angle \mathrm{C{-}C{-}H_{Me}}$, $\omega(\mathrm{C^2{=}C^3{-}C^4{-}H})$, $\angle \mathrm{C^1{-}C^5{-}H}$, $\omega(\mathrm{C^2{-}C^1{-}C^5{-}H})$, $\Delta[r(\mathrm{C{=}O}) - r(\mathrm{C{\equiv}C})]$, $\Delta[r(\mathrm{C^2{-}CH_3}) - r(\mathrm{C^1{-}C^2})]$, $\Delta[r(\mathrm{C^1{-}C^5}) - r(\mathrm{C^3{-}C^4})]$, $\Delta[r(\mathrm{C^4{-}C^5}) - r(\mathrm{C^3{-}C^4})]$.

ENONEN: $r(\mathrm{C{=}O})$, $r(\mathrm{C^6{=}C^7})$, $r(\mathrm{C^3{-}C^6})$, $r(\mathrm{C^3{-}C^4})$, $r(\mathrm{C_{sp^3}{-}H})$, $r(\mathrm{C_{sp^2}{-}H})$, $\angle \mathrm{C^2{-}C^3{-}C^4}$, $\angle \mathrm{C^1{-}C^2{-}C^3}$, $\angle \mathrm{C^2{-}C^1{=}O}$, $\angle \mathrm{C^2{=}C^3{-}C^6}$, $\angle \mathrm{C^3{=}C^2{-}CH_3}$, $\angle \mathrm{C^3{-}C^4{-}H}$, $\angle \mathrm{C{-}C{-}H_{Me}}$, $\omega(\mathrm{C^2{=}C^3{-}C^4{-}H})$, $\angle \mathrm{C^1{-}C^5{-}H}$, $\omega(\mathrm{C^2{-}C^1{-}C^5{-}H})$, $\angle \mathrm{C^3{-}C^6{=}C^7}$, $\angle \mathrm{C^7{=}C^6{-}H}$, $\omega(\mathrm{C^2{=}C^3{-}C^6{=}C^7})$, $\Delta[r(\mathrm{C^2{=}C^3}) - r(\mathrm{C^6{=}C^7})]$, $\Delta[r(\mathrm{C^1{-}C^2}) - r(\mathrm{C^3{-}C^6})]$, $\Delta[r(\mathrm{C^2{-}CH_3}) - r(\mathrm{C^3{-}C^6})]$, $\Delta[r(\mathrm{C^1{-}C^5}) - r(\mathrm{C^3{-}C^4})]$, $\Delta[r(\mathrm{C^4{-}C^5}) - r(\mathrm{C^3{-}C^4})]$.

ENONET: $r(\mathrm{C{=}O})$, $r(\mathrm{C^2{=}C^3})$, $r(\mathrm{C^1{-}C^2})$, $r(\mathrm{C^2{-}CH_3})$, $r(\mathrm{C^3{-}C^4})$, $r(\mathrm{C^6{-}C^7})$, $r(\mathrm{C_{sp^3}{-}H})$, $\angle \mathrm{C^2{-}C^3{-}C^4}$, $\angle \mathrm{C^1{-}C^2{-}C^3}$, $\angle \mathrm{C^2{-}C^1{=}O}$, $\angle \mathrm{C^2{=}C^3{-}C^6}$, $\angle \mathrm{C^3{=}C^2{-}CH_3}$, $\angle \mathrm{C^3{-}C^4{-}H}$, $\angle \mathrm{C{-}C{-}H_{Me}}$, $\omega(\mathrm{C^2{=}C^3{-}C^4{-}H})$, $\angle \mathrm{C^1{-}C^5{-}H}$, $\omega(\mathrm{C^2{-}C^1{-}C^5{-}H})$, $\angle \mathrm{C^3{-}C^6{-}C^7}$, $\omega(\mathrm{C^2{=}C^3{-}C^6{-}C^7})$, $\Delta[r(\mathrm{C^3{-}C^6}) - r(\mathrm{C^2{-}CH_3})]$, $\Delta[r(\mathrm{C^1{-}C^5}) - r(\mathrm{C^3{-}C^4})]$, $\Delta[r(\mathrm{C^4{-}C^5}) - r(\mathrm{C^3{-}C^4})]$.

Several small details from the *ab initio* calculations, *e.g.*, the differences in the methyl CCH angles, have been incorporated into the molecular models. Five of the parameters in all three models are valence and dihedral angles used to define the positions of the hydrogen atoms. Even if it were possible to include several of these in the refinements, the results would be relatively insensitive to these parameters, and in the final studies they were therefore fixed at the values calculated in the MP2/6-31G* optimisations.

The molecular structure parameters determined for the three derivatives of 2-methylcyclopent-2-enone from the gas electron diffraction studies are presented in Table 6. The results are based on the bond distance constraints listed in Table 5. Table 7 shows the results from least squares refinements when all parameters defining the positions of the heavy atoms were allowed to vary simultaneously. Due to high correlations

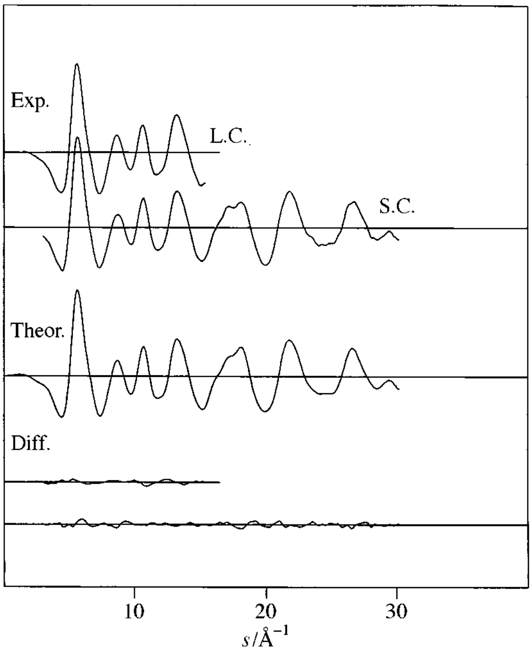

Fig. 2 Experimental and theoretical GED molecular intensities for 3-ethynyl-2-methylcyclopent-2-enone and their differences. The theoretical intensities are based on the structure parameters in Table 5.

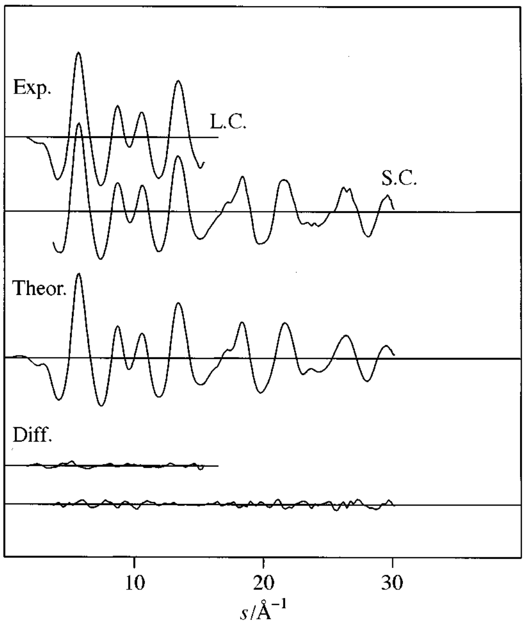

Fig. 3 Experimental and theoretical GED molecular intensities for 3-ethenyl-2-methylcyclopent-2-enone and their differences. The theoretical intensities are based on the structure parameters in Table 5.

between closely spaced bond distances these data are considered to be less reliable than those in Table 6. The standard deviations of the parameters are of course much higher in this case, and some of the parameters are clearly unreliable, for example $r(C^1–C^2)$ and $r(C^1–C^5)$ for ENONET. The experimental and final theoretical molecular intensity functions of the three molecules are shown in Figs. 2–4, while the corresponding radial distribution curves are presented in Figs. 5–7. The theoretical intensity and radial distribution curves are calculated from the parameters listed in Table 6.

Discussion

The gas electron diffraction studies of the three substituted cyclopent-2-enone molecules show that they all have planar

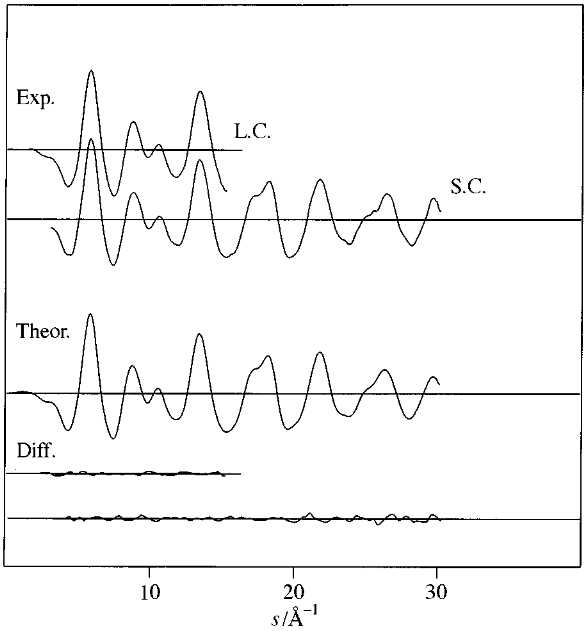

Fig. 4 Experimental and theoretical GED molecular intensities for 3-ethyl-2-methylcyclopent-2-enone and their differences. The theoretical intensities are based on the structure parameters in Table 5.

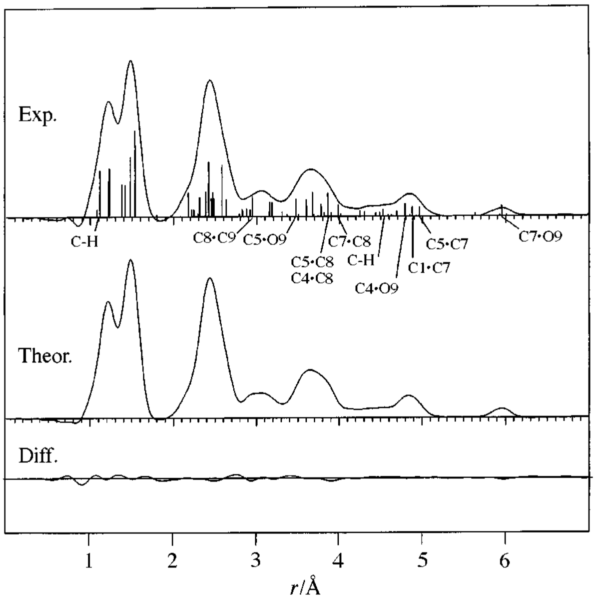

Fig. 5 Experimental and theoretical radial distribution curves for 3-ethynyl-2-methylcyclopent-2-enone and their differences. The theoretical curve is based on the structure parameters in Table 5.

five-membered rings, in agreement with results from the *ab initio* calculations. For ENONYN the conformer with the ethynyl group being coplanar with the ring is the only one attainable.

The observed ENONEN conformer has the ethenyl substituent in an s-*trans* orientation relative to the C=C bond in the ring. This is reasonable, as 1,3-diene systems generally show strong preference for s-*trans* conformations. In the present case an s-*cis* conformation of the substituent group would furthermore be destabilised due to steric repulsions between the 3-ethynyl and 2-methyl substituents.

In ENONET the ethyl substituent assumes a skew (*gauche*) orientation relative to the C=C bond in the ring. This is in accordance with the preferred conformation (83%) of but-1-ene.[15] In ENONET the alternative conformer, with the ethyl group being eclipsed with the C=C bond, would be further destabilised, relative to that of but-1-ene, due to van der Waal's

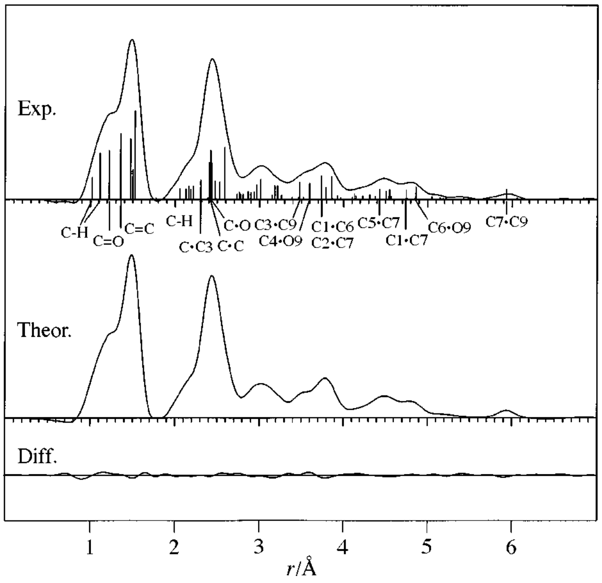

Fig. 6 Experimental and theoretical radial distribution curves for 3-ethenyl-2-methylcyclopent-2-enone and their differences. The theoretical curve is based on the structure parameters in Table 5.

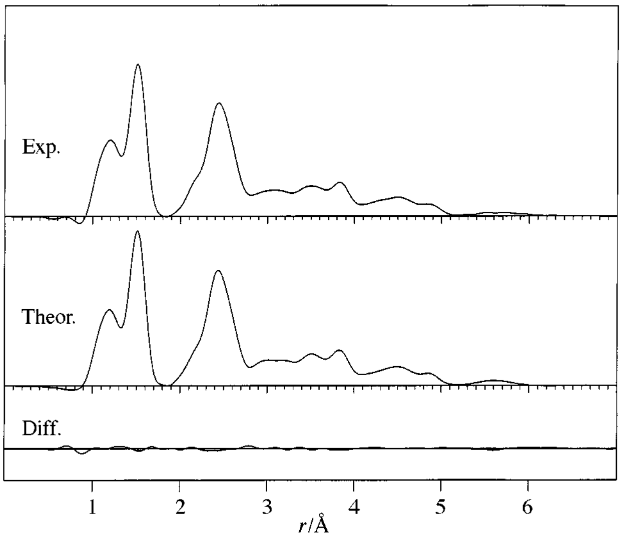

Fig. 7 Experimental and theoretical radial distribution curves for 3-ethyl-2-methylcyclopent-2-enone and their differences. The theoretical curve is based on the structure parameters in Table 5.

interactions between the 2-methyl and 3-ethyl substituents. It is therefore reasonable that the skew (*gauche*) conformer is the only one present.

If the observed GED structure parameters for the three cyclopentenone molecules, see Table 6, are compared to those observed for the simplest conjugated carbonyl compound, acrolein, from MW[16] and GED[17] studies, [(*r*(C=C): 1.341 Å[16]; 1.345 Å,[17] *r*(C–C): 1.468 Å;[16] 1.484 Å,[17], *r*(C=O): 1.215 Å;[16] 1.217 Å[17]], it will be noted that the C=C bond—and to a smaller extent the C=O bond—in the former is significantly longer than the corresponding bond in acrolein, indicating substantial increased π electron delocalization in these molecules. This is not, however, an adequate description of the structures of the three cyclopentenone molecules, as enlarged C=C and C=O bonds are also observed for ENONET, where the 3-substituent is an (unconjugative) ethyl group. It is reasonable to describe the lengthened C=C bond in the ring as a result of enforced reduction in the optimal C–C=C angles due to the formation of the ring. This could be interpreted in terms of rehybridization of the ring carbon atoms, giving less s-character to the σ orbitals of the C=C bonds, or alternatively as formation of bent σ bonds, both descriptions being in accordance with lengthened C=C bonds.

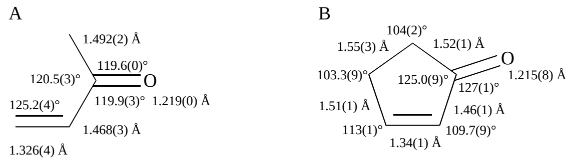

Fig. 8 Average bond lengths/Å and bond angles/° with standard deviations from X-ray structure determinations of 2 noncyclic (A) and 26 cyclic (B) conjugated enones[2]

The interpretation above is supported by results from X-ray structure studies of acyclic and cyclic enones, as reported in ref. 2. Fig. 8 shows averaged observed bond lengths and bond angles of the enone fragment of two aliphatic acyclic enones (A) and similar data for the cyclopentenone fragment, based on 26 XR structures (B). When the enone carbon fragment is part of a cyclopentenone ring, the valence angles of the enone fragment are highly affected. This is especially noticable for $\angle C^1–C^2=C^3$, where the angle is decreased by 15.5° relative to that in the acyclic enone. When we compare the bond lengths for the two types of structure, the most pronounced difference is observed for the C=C bond, which is 0.01–0.02 Å larger in the cyclic enone, in good agreement with the results from the GED studies.

The differences in comparable parameters observed for the cyclopentenones molecules studied by GED, see Table 6, are small and of similar order of magnitudes as the error limits of the observed parameters. It is therefore not possible to draw definite conclusions regarding the effects from the three 3-substituents based on the observed GED data alone. The structures will therefore be discussed in conjunction with interpretations based on results from hydrogenation measurements and on MP2/6-31G* *ab initio* calculations carried out for structurally related molecules.

There are several probes of the conjugation energy of the ethynyl, ethenyl and ethyl enones. We start our analysis with the less conjugated species so as to decouple the variously conjugated groups. In particular, let us 'delete' the carbonyl group (and the five-membered ring) and discuss derivatives of the type $(Z)\text{–}CH_3\text{–}CH{=}CHR$ for R = $–C{\equiv}CH$, $–CH{=}CH_2$ and $–CH_2CH_3$ with regards to the conjugative interactions of the C=C double bond with the R group. A simple probe is the comparison of the hydrogenation enthalpies of $(Z)\text{–}CH_3CH{=}CHR$ to the corresponding $CH_3CH_2CH_2R$, *i.e.* the enthalpies of the three reactions (1):

$$(Z)\text{-}CH_3\text{–}CH{=}CHR(g) + H_2(g) \longrightarrow CH_3\text{–}CH_2\text{–}CH_2R(g) \quad (1)$$

Making use of the enthalpy of formation data from ref. 18 (our standard source unless otherwise stated), we find that the three reaction enthalpy values are −27.7,[19] −24.5 and −28.5 kcal mol^{-1}. The difference of the ethynyl and ethenyl values from that of the ethyl may be viewed as the additional conjugation energy of the enyne and diene. These are 0.8 and 4.0 kcal mol^{-1}, respectively. Alternatively, we note that the numerical similarity of the values of reaction enthalpy from ethynyl and ethyl, as opposed to that of ethynyl, suggest that the ethynyl substituent will have considerably less conjugative interaction with the enone than does the ethenyl substituent.

An alternative set of reactions is:

$$(Z)\text{-}CH_3\text{–}CH{=}CHR(g) + C_2H_6(g) \longrightarrow (Z)\text{–}CH_3\text{–}CH{=}CHCH_3(g) + RCH_3(g) \quad (2)$$

From the same sources for enthalpies of formation, we find the three reaction enthalpy values are 0.6, 3.7 and −0.1 kcal $^{-1}$, in agreement with ethynyl conjugating considerably less than ethenyl, where the enyne and diene conjugation energies are 0.5 and 3.6 kcal mol^{-1}, respectively.

As the enthalpies of formation for all three CH_3–CH=CHR species are known for the (*E*)-isomers as well, these related reaction enthalpies may also be studied, and we therefore replace reactions (1) and (2) by reactions (3) and (4).

$$(E)\text{-}CH_3\text{–}CH{=}CHR(g) + H_2(g) \longrightarrow CH_3\text{–}CH_2\text{–}CH_2R(g) \quad (3)$$

$$(E)\text{-}CH_3\text{–}CH{=}CHR(g) + C_2H_6(g) \longrightarrow (E)\text{-}CH_3\text{–}CH{=}CHCH_3(g) + RCH_3(g) \quad (4)$$

The experimental enthalpies of reactions (3) are −27.5,[19] −23.3 and −27.5 kcal mol^{-1}, while the three reaction enthalpies of reactions (4) are −0.4, 3.9 and −0.1 kcal mol^{-1}. These data do therefore support those presented above, regarding the conjugative effects from ethynyl and ethenyl groups.

There are several other unsaturated substructures of the enones where similar data would be of interest. We may for example want to mimic the effect of the substituents on the C=C−C=O substructure of the substituted cyclopentenones, corresponding to the reactions (5) and (6).

$$(E)\text{-}O{=}CH\text{−}CH{=}CHR(g) + H_2(g) \longrightarrow O{=}CH\text{−}CH_2\text{–}CH_2R(g) \quad (5)$$

$$(E)\text{-}O{=}CH\text{−}CH\text{−}CHR(g) + C_2H_6(g) \longrightarrow (E)\text{-}O{=}CH\text{−}CH{=}CHCH_3(g) + RCH_3(g) \quad (6)$$

However, in this case, there are no experimentally available measurements for the enthalpy of formation of any of these β-substituted acroleins. The same is true for other related substructures.

Ab initio calculations can provide a tool for investigating energy changes for reactions in which the π electron conjugation between two unsaturated systems is disrupted (R = C≡CH, −CH=CH_2) and comparing them with the energy changes for similar reactions in systems which do not experience disruption (R = CH_2–CH_3). In reactions (1), (3) and (5), the conjugation is broken by hydrogenating the substituted C=C bond, and in reactions (2), (4) and (6), the same is accomplished by exchanging R with a methyl group, *i.e.* by splitting the two π systems (R = C≡CH, −CH=CH_2). Such calculations have been carried out for reactions (1)–(6) shown above, as well as for the following relevant reactions (7)–(10):

$$CH_2{=}CHR(g) + H_2(g) \longrightarrow CH_3\text{–}CH_2R(g) \quad (7)$$

$$CH_2{=}CHR(g) + C_2H_6(g) \longrightarrow CH_2{=}CHCH_3(g) + RCH_3(g) \quad (8)$$

$$(Z)\text{-}O{=}CH\text{−}CH{=}CHR(g) + H_2(g) \longrightarrow O{=}CH\text{−}CH_2\text{–}CH_2R(g) \quad (9)$$

$$(Z)\text{-}O{=}CH\text{−}CH{=}CHR(g) + C_2H_6(g) \longrightarrow (E)\text{-}O{=}CH\text{−}CH{=}CHCH_3(g) + RCH_3(g) \quad (10)$$

$$(E)\text{-}O{=}CH\text{−}C(CH_3){=}CHR(g) + C_2H_6(g) \longrightarrow (E)\text{-}O{=}CH\text{−}C(CH_3){=}CHCH_3(g) + RCH_3(g) \quad (11)$$

$$\text{ENONYN(ENONEN; ENONET)}(g) + C_2H_6(g) \longrightarrow \text{2,3-Dimethylcyclopent-2-enone}(g) + RCH_3(g) \quad (12)$$

Table 8 presents the reaction enthalpies for the hydrogenation reactions (1), (3), (5), (7) and (9), as calculated from the *ab initio* MP2/6-31G* energies of the molecules involved, see Table 3.

Table 8 Reaction enthalpies (kcal mol^{-1}) for hydrogenation reactions aimed at elucidating the effect of conjugation from −C≡C−H and −CH=CH_2 substituents on enone systems, as calculated from the energies of *ab initio* MP2/6-31G* optimized structures

		R		
Reaction	Molecule[a]	−C≡C−H	−CH=CH_2	−CH_2–CH_3
(1)	14 + 1 ⟶ 16	−32.3		
	17 + 1 ⟶ 19		−32.4	
	20 + 1 ⟶ 22			−36.6
(3)	13 + 1 ⟶ 16	−32.8		
	18 + 1 ⟶ 19		−30.8	
	21 + 1 ⟶ 22			−35.0
(5)	27 + 1 ⟶ 28	−28.2		
	30 + 1 ⟶ 34		—	
	32 + 1 ⟶ 35			−30.0
(7)	6 + 1 ⟶ 8	−36.2		
	7 + 1 ⟶ 9		−34.1	
	9 + 1 ⟶ 12			−38.1
(9)	26 + 1 ⟶ 28	−29.1		
	29 + 1 ⟶ 34		—	
	31 + 1 ⟶ 35			−32.9

[a] The numbers refer to the molecules listed in Table 3.

Table 9 Reaction enthalpies (kcal mol^{-1}) for substitution reactions aimed at elucidating the effect of conjugation from −C≡C−H and −CH=CH_2 substituents on enon systems, as calculated from the energies of *ab initio* MP2/6-31G* optimized structures

		R		
Reaction	Molecule[a]	−C≡C−H	−CH=CH_2	−CH_2–CH_3
(2)	14 + 2 ⟶ 10 + 3	4.6		
	17 + 2 ⟶ 10 + 4		4.4	
	20 + 2 ⟶ 10 + 5			−0.1
(4)	13 + 2 ⟶ 11 + 3	2.9		
	18 + 2 ⟶ 11 + 4		4.5	
	21 + 2 ⟶ 11 + 5			0.1
(6)	27 + 2 ⟶ 24 + 3	0.9		
	30 + 2 ⟶ 24 + 4		4.2	
	32 + 2 ⟶ 24 + 5			0.1
(8)	6 + 2 ⟶ 4 + 3	1.9		
	7 + 2 ⟶ 4 + 4		4.0	
	9 + 2 ⟶ 4 + 5			0.0
(10)	26 + 2 ⟶ 23 + 3	2.9		
	29 + 2 ⟶ 23 + 4		4.2	
	31 + 2 ⟶ 23 + 5			0.1
(11)	36 + 2 ⟶ 33 + 3	3.3		
	37 + 2 ⟶ 33 + 4		4.6	
	38 + 2 ⟶ 33 + 5			0.1
(12)	40 + 2 ⟶ 39 + 3	2.9		
	41 + 2 ⟶ 39 + 4		3.8	
	42 + 2 ⟶ 39 + 5			−0.1

[a] The numbers refer to the molecules listed in Table 3.

Similar data for the substitution reactions (2), (4), (6), (8), (10), (11) and (12) are shown in Table 9. With the exception of reactions (1) and (2), where the calculated reaction enthalpies are approximately the same for ethynyl and ethenyl substituents, all the other reaction enthalpies are in agreement with the experimental results for reactions (1)–(4), namely that the ethynyl substituent has considerably less conjugative interaction with the enone—or other π system—than does the ethenyl substituent. From the hydrogenation reactions in Table 8 the conjugative effect of the vinyl group is calculated to be 4.2, 4.2 and 4.0 kcal mol^{-1}, corresponding to an average of 4.1 kcal mol^{-1}, while that calculated for the ethynyl group shows much larger variations, namely 4.3, 2.2, 1.8, 1.9, 3.8 kcal mol^{-1}, with an average of 2.8 kcal mol^{-1}, or 2.4 kcal mol^{-1} if the data for reaction (1) is omitted. The conjugative effect from the two unsaturated groups may similarly be estimated from the calculated reaction enthalpies shown in Table 9, which for the vinyl group is 4.5, 4.4, 4.1, 4.0, 4.1, 4.5 kcal mol^{-1}, with an average of

4.3 kcal mol^{-1}, and for the ethynyl group is 4.7, 2.8, 0.8, 1.9, 2.8, 3.2 kcal mol^{-1}, with an average of 2.7 kcal mol^{-1}, or 2.3 kcal mol^{-1} if the data for reaction (2) is excluded. These data indicate that the conjugative effect of a vinyl group is approximately 4.2 kcal mol^{-1}, in agreement with experimental results from the hydrogenation measurements referred to above, and that the conjugative effect from an ethynyl group is more variable, but on an average *ca.* 2.0 kcal mol^{-1} lower than that of the vinyl group.

Unfortunately it is not possible to detect any differences in the observed structures of the three cyclic enones (Table 6) that might be ascribed to the difference in conjugative effect between an ethynyl (ENONYN) and an ethenyl (ENONEN) substituent. The calculated energy difference between the two groups, see Table 9, is only 0.9 kcal mol^{-1} for reaction (12), and the energies of these cyclic molecules might therefore be influenced also by other forces. The structure parameters that probably will be most affected by a difference in conjugative effect are the $C^2{=}C^3$ and $C^1{-}C^2$ bonds. According to the *ab initio* structures of the three enone molecules (Table 2), the $C^2{=}C^3$ bonds in ENONYN and ENONEN are 0.0045 Å and 0.0066 Å longer than that in ENONET, and the differences in the calculated $C^1{-}C^2$ bond lengths are even smaller. As these differences are smaller than the combined standard deviations of the observed structures, it is not surprising that these effects cannot be documented by the observed GED structures.

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