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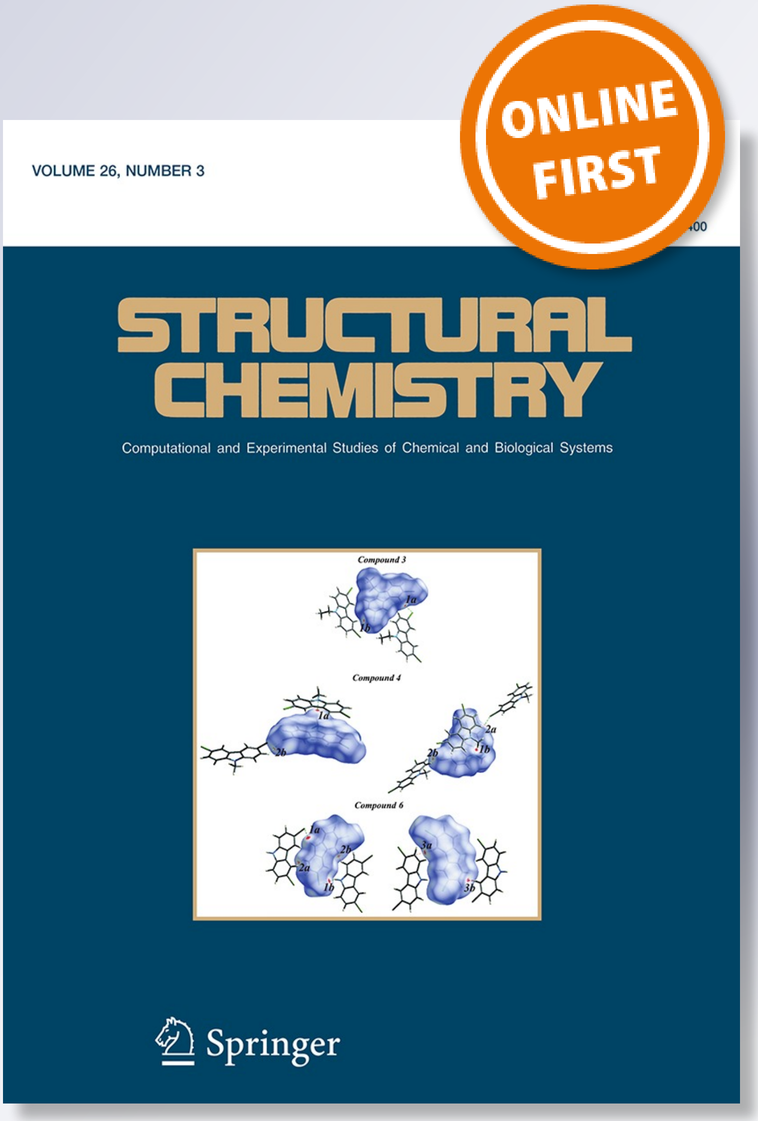

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ORIGINAL RESEARCH

Theoretical characterization of the chemical bonds of some three-membered ring compounds through QTAIM theory

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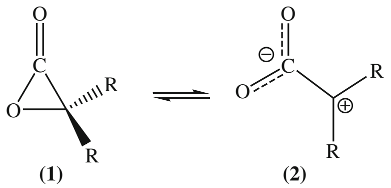
Abstract In this paper, we investigate the nature of the carbonyl and the intraring C–C, C–N, C–O, N–N, O–O and N–O bonds of cyclopropanone and the following cyclopropanone derivatives: aziridine-2-one (**1**); oxirane-2-one (**2**); 1,2-diaziridine-3-one (**3**); 1,2-dioxirane-3-one (**4**); 1,2-oxaziridine-3-one (**5**); cyclopropane-1,2-dione (**6**); aziridine-2,3-dione (**7**); and oxirane-2,3-dione (**8**). The intramolecular distribution of the electronic charge density and the $L(\mathbf{r}) = -\frac{1}{4}\nabla^2\rho(\mathbf{r})$ function have been investigated within the framework of the quantum theory of atoms in molecule theory. This methodology allowed us to characterize the bonds of cyclopropanone and the cyclopropanone derivatives studied here.

Keywords Cyclopropanone · Cyclopropanone derivatives · Electronic charge density · Laplacian · QTAIM analysis

Introduction

Cyclopropanone and its derivatives are highly reactive organic compounds containing labile bonds on a small cyclic skeleton. The chemistry of cyclopropanones is of considerable interest because of their reactivity and great potential as intermediates in organic syntheses [1, 2]. In addition, the chemistry of small-ring heterocycles as oxiranes (epoxides) and aziridines is too of interest since they are among the most widely used intermediates in organic synthesis [3–6]. Moreover, α-lactones (oxiran-2-ones) are three-membered heterocyclic rings that have been invoked as intermediates in a variety of organic reactions [7–10]. Many of the chemical reactions of the α-lactones have been explained by invoking a higher-energy ring-opened zwitterionic form (**2**). The relative stability of ring-closed form (**1**) versus ring-opened form (**2**) is dependent on the substituent R. Calculations have predicted that for the parent α-lactone (R=H), ring-closed form (**1**) is significantly lower in energy than ring-opened form (**2**) [11–15].



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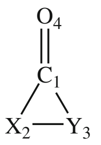
It is well known that an exocyclic double bond increases the ring strain energy of three-membered rings carbocycles and heterocycles [16–18]. Wiberg et al. [19], through measurements of the enthalpies of combustion, estimated strain energy for methylenecyclopropane about 56 kJ mol^{-1} greater than that for cyclopropane. Rodriquez et al. [20] estimated that cyclopropanone is about 66 kJ mol^{-1} more strained than cyclopropane and calculated oxirane-2-one to have a ring strain energy 55 kJ mol^{-1} greater than that of oxirane (ethylene oxide). Turning to endocyclic double bonds, Johnson and Borden [17] and Wiberg et al. [19] suggested the strain energy of cyclopropene is ca. 110 kJ mol^{-1} more than cyclopropane, a value consonant with the results discussed by Johnson and Borden [17], and Liebman and Greenberg [21 (references cited therein)]. It is a good generalization that each trigonal carbon in a three-membered ring contributes some ca. 60 kJ mol^{-1}.

Ruggiero et al. through the topological analysis of the electron charge density analyzed oxiranone and hydroxyoxiranone and compared them with cyclopropane, cyclopropanone and oxirane [22, 23]. They concluded that oxiranone may be considered as an α-lactone that has considerable ionic character in the endocyclic C_α–O (C_1–O_2) bond (see Scheme 1 for the atom numbering).

Moreover, Ho et al. [24] have investigated through the π-complex-back-donation model (π-cbd) and the quantum theory of atoms in molecules (QTAIM) the C–C and C–O bond lengths in oxirane and derivatives. These researchers found that the shortenings of the C–C bond in the oxirane ring and of the neighboring C–C bond arise mainly from the substituent groups. However, neither the π-cbd model nor the QTAIM offer a satisfactory explanation for the elongation of the intraring C–O bonds.

In a recent work, we have studied the structure and energetics of the related molecules: aziridine-2-one (**1**); oxirane-2-one (**2**); 1,2-diaziridine-3-one (**3**); 1,2-dioxirane-3-one (**4**); 1,2-oxaziridine-3-one (**5**); cyclopropane-1,2-dione (**6**); aziridine-2,3-dione (**7**); and oxirane-2,3-dione (**8**) [25]. To the best of our knowledge, the nature of the interatomic interactions in the cyclopropanone derivatives mentioned is at best poorly known. In order to assess the strength of the bonds, we have analyzed local topological properties at the bond critical points (BCP) within the framework of the QTAIM, comparing with the properties of conventional bonds not emphasized. This theory has recently been used to estimate ring strain energies of unsaturated rings including cycloketones [26]. In what follows, we will refer to compounds with a carbonyl group and a three-membered ring as "cyclopropanone derivatives" regardless of any heteroatom in that ring.



X_2 = NH, O or CH_2

Y_3 = CH_2, NH, O or CO

Scheme 1 Atom numbering scheme of the cyclopropanone derivatives

Computational details

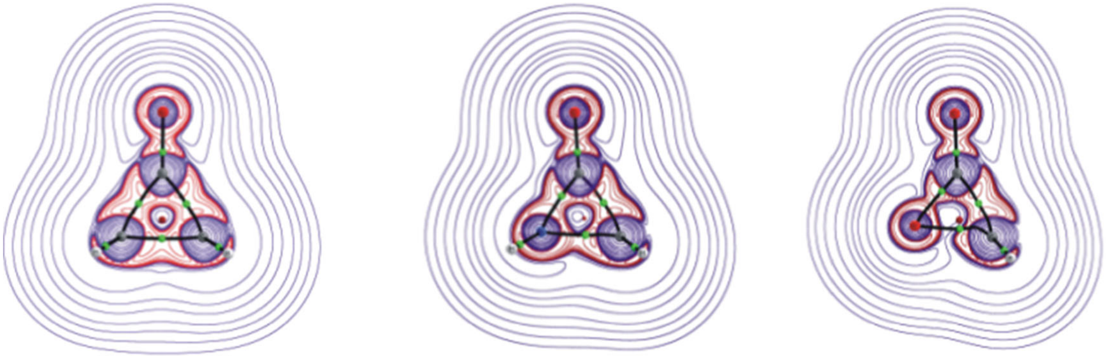
The geometries of cyclopropanone derivative molecules were taken from ref. [25] and optimized again using the Møller–Plesset second-order (MP2) perturbation theory [27] with the 6-311++G(2d,2p) basis set. Conventional, i.e., related acyclic, molecules were used for comparison with the properties of species with unstrained covalent bonds. All of these cyclic and acyclic molecules were optimized at the same level of theory. The corresponding harmonic vibrational frequencies were computed at the same level of theory as the optimized structures. The frequency calculations found that the examined structures have no imaginary vibrational frequencies showing these species are energy minima, although not necessarily the absolute minimum [cf. species (**6**) is less stable than its *syn*- and *anti*-enol tautomers]. All calculations were performed with Gaussian 09 [28].

A QTAIM analysis [29–31] was carried using the AIMAll [32] software, with the electron density generated at the MP2/6-311++G(2d,2p) level of theory.

Results and discussion

The topological analysis of the electron density, $\rho(\mathbf{r})$, and its Laplacian function, $\nabla^2\rho(\mathbf{r})$, constitute a powerful tool to investigate the nature of the chemical bonds [29]. According to Bader theory, the presence of a bond path (BP) is a universal indicator of the existence of a bonding interaction [33]. Figure 1 shows the molecular graphs and the contour maps of $L(\mathbf{r}) = -\frac{1}{4}\nabla^2\rho(\mathbf{r})$ function for the molecules studied here (see Scheme 1 for the atom numbering). The parent carbocyclic cyclopropanone molecule was included for comparison between them. The expected network of BP linking pairs of neighboring nuclear attractors except in molecules (**4**) and (**5**) can be observed in Fig. 1.

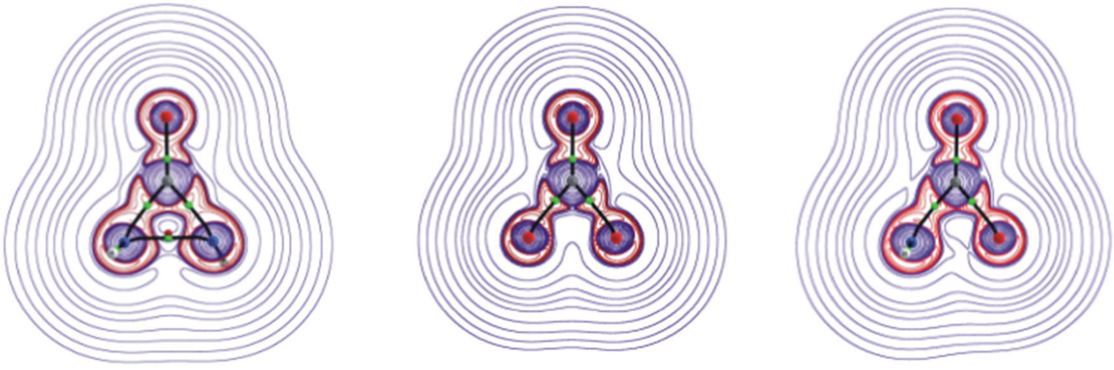
The $L(\mathbf{r})$ function is particularly relevant to the present work due to the fact that its topology shows the regions of the space where the electron density is locally concentrated [$L(\mathbf{r}) > 0$] or depleted [$L(\mathbf{r}) < 0$] [29, 30].



Cyclopropanone

Aziridine-2-one (**1**)

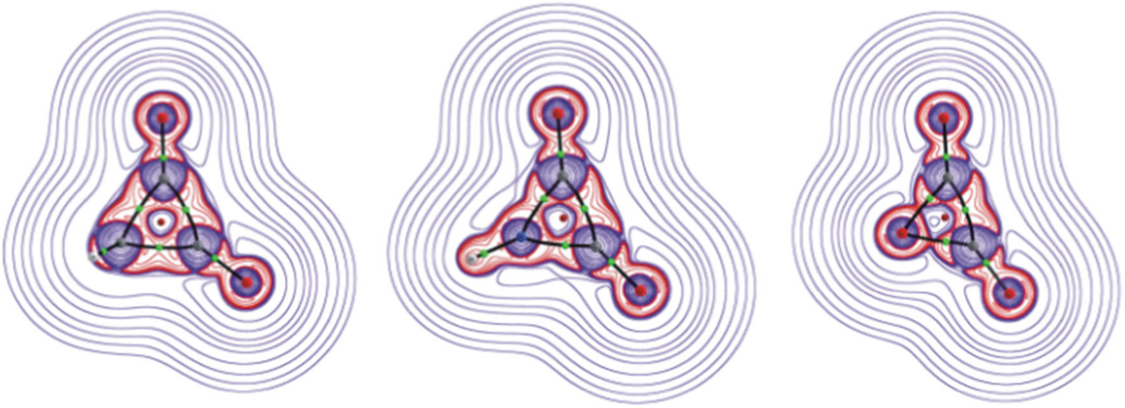
Oxirane-2-one (**2**)



1,2-diaziridine-3-one (**3**)

1,2-dioxirane-3-one (**4**)

1,2-oxaziridine-3-one (**5**)



Cyclopropane-1,2-dione (**6**)

Aziridine-2,3-dione (**7**)

Oxirane-2,3-dione (**8**)

Fig. 1 Contour map of $L(\mathrm{r}) = -\frac{1}{4}\nabla^2\rho(\mathrm{r})$ function for the studied molecules. *Blue lines* denote $L(\mathrm{r}) < 0$ and *red lines* $L(\mathrm{r}) > 0$. The *black lines* indicate the bond paths, and the *green* and *red dots* indicate the BCP and RCP, respectively, of the $\rho(\mathrm{r})$ topology (Color figure online)

According to QTAIM, when the electron charge density is shared by both nuclei, as is found in interactions usually characterized as covalent, these are shared-shell interactions. In these interactions, it is observed that the region of space over which the $L(\mathbf{r})$ function is positive and which contains the BCP is contiguous over the valence regions of both atoms. The second limiting of atomic interaction is when the electron charge density is not shared by both nuclei; these are the closed-shell interactions. In Fig. 1, it is observed that for all interatomic interactions C_1–O_4, C_1–X_2 and C_1–Y_3 the $L(\mathbf{r})$ function presents a continuous accumulation region of charge density between the interacting atoms. In other words, the C_1–O_4, C_1–X_2 and C_1–Y_3 interactions are covalent bonds. The X_2–Y_3 bonds are shared-shell interactions in (**1**), (**6**), (**7**) and (**8**) molecules. However, for the O_2–C_3 and N_2–N_3 bonds in molecules (**2**) and (**3**), respectively, despite not having a continuous accumulation region of charge density between the interacting nuclei, a polarization of the valence shell concentration charge (VSCC) of both atoms in direction of the bond path is observed. That is, it seems that there is a tendency to form continuous accumulation region of charge density between the interacting nuclei.

In other words, the X_2–Y_3 bonds in (**1**), (**6**), (**7**) and (**8**) molecules are true covalent bonds, while in (**2**) and (**3**) molecules the X_2–Y_3 bonds are very strained. Moreover, in molecules (**4**) and (**5**), it is not observed either a continuous accumulation region of charge density or a polarization of the VSCC of both atoms in direction of the X_2 and Y_3 nuclei. The local topological properties at the bond critical point (BCP) can be used to describe the strength of a bond, especially when the same pair of atoms is interacting. In general, the larger the magnitudes of $\rho(\mathbf{r}_b)$, $\nabla^2\rho(\mathbf{r}_b)$ and $H(\mathbf{r}_b)$, the stronger the bond. Table 1 reports selected local topological properties calculated at the BCP of the optimized molecular structures of the molecules studied here. According to QTAIM analysis, these parameters reveal the nature of the interatomic interactions. It is observed from Table 1 that all interatomic interactions C_1–O_4, C_1–X_2 and C_1–Y_3 present values typical of shared-shell interactions: The values of $\rho(\mathbf{r}_b)$ are relatively large, and the values of $\nabla^2\rho(\mathbf{r}_b)$ and $H(\mathbf{r}_b)$ are relatively large and negative. That is, there are no doubts that the C_1–O_4, C_1–X_2 and C_1–Y_3 interactions are covalent bonds. In return, the X_2–Y_3 interactions are more complex and will be discussed later. In order to assess the strength of the bonds, next we have analyzed local topological properties at the C_1–O_4, C_1–X_2, C_1–Y_3 and X_2–Y_3 BCPs, comparing with the properties of conventional not strained covalent bonds.

C_1–O_4 bond

It can be seen that in all molecules the C_1–O_4 interatomic distance is slightly shorter than a C–O double covalent bond and longer than a C–O triple covalent bond. In the molecules studied here, the C–O interatomic distances range from 1.179 to 1.207 Å, while $d_{C=O} = 1.212$ Å in methyl acetate and $d_{C\text{–}O} = 1.138$ Å in carbon monoxide.

Topological parameters $\rho(\mathbf{r}_b)$ and $H(\mathbf{r}_b)$ enable us to characterize the C_1–O_4 bonds. In all molecules studied here, these topological properties at the C_1–O_4 BCPs (see Table 1) are higher in magnitude than the values found in C–O double covalent bonds [i.e., $\rho(\mathbf{r}_b) = 0.4059$ au and $H(\mathbf{r}_b) = -0.7387$ au in acetone] and are lower in magnitude than the values found in C–O triple covalent bonds [i.e., $\rho(\mathbf{r}_b) = 0.4935$ au and $H(\mathbf{r}_b) = -0.9532$ au in carbon monoxide].

Moreover, the bond order n of the C_1–O_4 bond has also been examined within the framework of QTAIM [29] $n = \exp[A\rho(\mathbf{r}_b) - B]$, where $A = 4.5561$ and $B = 1.1523$. Surprisingly, for all molecules studied here, the bond order n denotes a higher double-bond character.

Moreover, it is well known that the stretching vibration frequency is a measure of the strength of a chemical bond. Table 1 presents stretching vibration frequency of the C_1–O_4 bond in our diverse species. It is observed that the shortening of the C_1–O_4 bond, with respect to a conventional C–O double covalent bond ($d_{C\text{–}O} = 1.220$ Å in acetone), is accompanied by an increase in the strength of the C_1–O_4 bond ($\nu_{C\text{–}O} = 1745.15\ \mathrm{cm}^{-1}$ in acetone). This idea is supported by the analysis of the bond order n of the QTAIM theory. All the more, Fig. 2 shows a good correlation between the bond order and the stretch vibration frequency of the C_1–O_4 bond. The vibration frequencies of molecules (**6**), (**7**) and (**8**) have not been included in the correlation because they do not have a pure vibrational mode for the C_1–O_4 bond. In these molecules, there are two frequencies associated with the stretching of the C=O bonds. It is observed that ν_{strech} sym is greater than ν_{strech} asym. These values are explained probably in terms of the coupling between the carbonyl groups and are assigned to symmetric and asymmetric stretching vibrational motions. The joint analysis of the interatomic distances, the vibrational frequencies and the local topological properties measured at the C_1–O_4 BCPs show that the C_1–O_4 bonds are stronger than a conventional C–O double bond.

C_1–X_2 bond

In molecules (**1**), (**3**), (**5**) and (**7**), the C_1–N_2 interatomic distance ranges from 1.371 to 1.414 Å. These values are intermediate between a single bond ($d_{C\text{–}N} = 1.467$ Å in methanamine) and double bond ($d_{C\text{–}N} = 1.277$ Å in methanimine) and are on the same order of magnitude of that of the partial double bonds in formamide ($d_{C\text{–}N} = 1.439$ Å).

The topological properties at the C_1–N_2 BCPs (see Table 1) show similar trends. That is, $\rho(\mathbf{r}_b)$ and $H(\mathbf{r}_b)$ are lower in magnitude than the values found in C–N double covalent bonds [i.e., $\rho(\mathbf{r}_b) = 0.3935$ au and $H(\mathbf{r}_b) = -0.6827$ au in methanimine] and higher in magnitude than the values found in C–N single covalent bonds [i.e., $\rho(\mathbf{r}_b) = 0.2669$ au and $H(\mathbf{r}_b) = -0.2999$ au in methanamine]. These findings suggest that the C_1–N_2 bonds have an intermediate character between single and double bonds, despite the nonplanarity of the N_2 atom in (**1**), (**3**) and (**5**) molecules.

C_1–O_2/O_3 bond

In (**2**), (**4**) and (**5**) molecules, the C_1–O_2/O_3 bonds are stronger than the C–O single bond in methanol [i.e., $d_{C\text{–}O} = 1.427$ Å, $\rho(\mathbf{r}_b) = 0.2526$ au and $H(\mathbf{r}_b) = -0.3771$ au] and are slightly stronger than the C–O single bond in formic acid [i.e., $d_{C\text{–}O} = 1.357$ Å, $\rho(\mathbf{r}_b) = 0.3013$ au and $H(\mathbf{r}_b) = -0.4800$ au]. In molecule (**8**), the C_1–O_2 bond is slightly weaker than the C–O single bond in methanol.

Table 1 Selected interatomic distances (Å), computed frequencies (cm^{-1}) and topological parameters (atomic units, except n that is dimensionless)

Molecule	Bond	d	ν_{strech}	Topological parameters			
				$\rho(\mathbf{r}_b)$	$\nabla^2\rho(\mathbf{r}_b)$	$H(\mathbf{r}_b)$	n
Cyclopropanone	C_1–O_4	1.204	1877.19	0.4126	−0.1835	−0.7489	2.07
	C_1–C_2	1.471		0.2587	−0.5369	−0.2305	
	C_1–C_3						
	C_2–C_3	1.583		0.2009	−0.2222	−0.1381	
1	C_1–O_4	1.201	1913.18	0.4182	−0.2682	−0.7636	2.12
	C_1–N_2	1.371		0.3128	−0.8643	−0.4026	
	C_1–C_3	1.470		0.2571	−0.5305	−0.2284	
	N_2–C_3	1.545		0.2100	−0.1869	−0.1707	
2	C_1–O_4	1.192	1958.91	0.4287	−0.2610	−0.7908	2.23
	C_1–O_2	1.342		0.3071	−0.6093	−0.4816	
	C_1–C_3	1.450		0.2699	−0.6225	−0.2509	
	O_2–C_3	1.552		0.1944	0.0212	−0.1565	
3	C_1–O_4	1.191	1943.26	0.4292	−0.2465	−0.7924	2.23
	C_1–N_2	1.393		0.3032	−0.7877	−0.3563	
	C_1–N_3						
	N_2–N_3	1.626		0.1871	0.2946	−0.0932	
4	C_1–O_4	1.179	2009.95	0.4438	−0.2390	−0.8313	2.39
	C_1–O_2	1.342		0.3105	−0.7415	−0.4867	
	C_1–O_3						
	O_2–O_3	1.631		Not found			
5	C_1–O_4	1.185	1973.72	0.4364	−0.2552	−0.8117	2.31
	C_1–N_2	1.406		0.2971	−0.7611	−0.3374	
	C_1–O_3	1.331		0.3159	−0.6725	−0.5042	
	N_2–O_3	1.635		Not found			
6	C_1–O_4	1.201	1761.34 asym	0.4146	−0.1294	−0.7552	2.09
	C_1–C_2	1.531	1841.59 sym	0.2339	−0.4007	−0.1844	
	C_2–C_3						
	C_1–C_3	1.494		0.2454	−0.4576	−0.2032	
7	C_1–O_4	1.192	1816.21 asym	0.4268	−0.2226	−0.7861	2.21
	C_1–N_2	1.414	1967.67 sym	0.2723	−0.5988	−0.3271	
	C_1–C_3	1.488		0.2471	−0.4414	−0.2068	
	N_2–C_3	1.414		0.2720	−0.5969	−0.3264	
8	C_1–O_4	1.179	1816.45 asym	0.4394	−0.1025	−0.8170	2.34
	C_1–O_2	1.443	2074.49 sym	0.2484	−0.3805	−0.2930	
	C_1–C_3	1.438		0.2733	−0.6137	−0.2547	
	O_2–C_3	1.443		0.2484	−0.3805	−0.2930	

d, interatomic distances; ν_{strech}, stretching vibration frequency of the C_1–O_4 bond; $\rho(\mathbf{r}_b)$, electron charge density; $\nabla^2\rho(\mathbf{r}_b)$, Laplacian of the electron density; $H(\mathbf{r}_b)$, electronic energy density; n, bond order

C_1–Y_3 bond

The C_1–C_3 bond lengths in molecules (**1**), (**2**), (**6**), (**7**) and (**8**) are shorter than those of a C–C single covalent bond ($d_{C-C} = 1.496$ Å in 2-propenol). However, the topological properties $\rho(\mathbf{r}_b)$ and $H(\mathbf{r}_b)$ in general [except in (**8**)] are lower in magnitude than the C–C single covalent bond [i.e., $\rho(\mathbf{r}_b) = 0.2704$ au and $H(\mathbf{r}_b) = -0.2403$ au in 2-propenol]. That is, according to QTAIM analysis, the C_1–C_3 bond in molecules (**1**), (**2**), (**6**) and (**7**) is slightly weaker than a conventional C–C single covalent bond, as may be expected for strained and hence destabilized species.

X_2–Y_3 bond

To the best of our knowledge, the nature of the interatomic interactions X_2–Y_3 is little known. Figure 1 clearly shows the existence of a BCP and BP for every pair X_2–Y_3 except

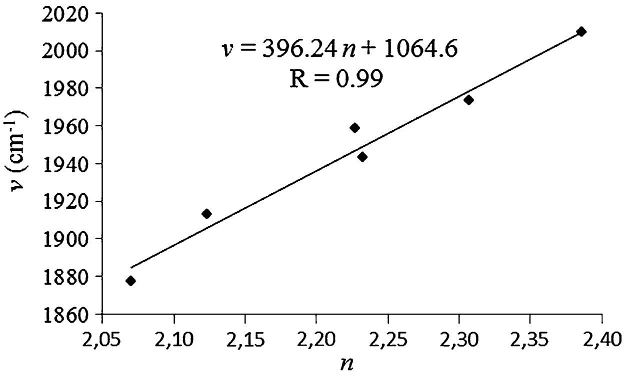


Fig. 2 Correlation between the vibrational frequencies and the bond order of the C_1–O_4 bond

for molecules (**4**) and (**5**). In molecule (**1**), the N_2–C_3 interatomic distance is 1.545 Å, being higher than the values found in N–C single covalent bonds ($d_{N–C} = 1.467$ Å in methanamine), while in molecule (**7**) is 1.414 Å. This interatomic distance is on the same order of magnitude of that of the partial double bond in formamide ($d_{N–C} = 1.430$ Å). In addition, structural analysis shows that the N_2 atom in (**1**) has a pyramidal arrangement, while the N_2 atom in (**7**) is planar. Concomitant with the decrease of the N–C distance, there is an increase in $\rho(\mathbf{r}_b)$ and $H(\mathbf{r}_b)$. In other words, the N_2–C_3 interatomic interaction in molecule (**1**) is a single covalent bond, somewhat unstable, while this interaction in molecule (**7**) has some double-bond character.

In molecule (**2**), the O_2–C_3 interatomic distance (1.552 Å) is longer than the O–C interatomic distance in methanol (1.427 Å). Local topological parameters show that at the O_2–C_3 BCP $\rho(\mathbf{r}_b)$ is relatively large, $\nabla^2\rho(\mathbf{r}_b) < 0$ and $H(\mathbf{r}_b) < 0$, which is indicative of a shared-shell interaction. However, these parameters are significantly lower than those in methanol [i.e., $\rho(\mathbf{r}_b) = 0.2526$ au, $\nabla^2\rho(\mathbf{r}_b) = -0.4812$ au and $H(\mathbf{r}_b) = -0.3771$ au]. Based on the foregoing discussion, the O_2–C_3 bond may be considered as a weak single covalent bond. These results do not agree with those reported by Ruggiero et al. [22, 23]. These researchers considered that this bond is essentially of ionic character.

The N_2–N_3 bond in (**3**) (1.626 Å) is longer than the N–N bond in hydrazine (1.481 Å). Structural analysis shows that both nitrogen atoms have a pyramidal structure as in hydrazine. QTAIM analysis shows that $\nabla^2\rho(\mathbf{r}_b) > 0$ and $H(\mathbf{r}_b) < 0$ at the BCP of this bond, which is indicative of a closed-shell interaction, while in hydrazine both parameters are negative at the N–N BCP. In other words, the N_2–N_3 bond in (**3**) is weaker than a conventional N–N bond.

In molecule (**4**), the distance between O_2 and O_3 (1.631 Å) is substantially shorter than the distances between O_2 and O_4, and O_3 and O_4 (2.388 Å). Something similar happens in molecule (**5**), and the distance between N_2 and O_3 (1.635 Å) is shorter than the distance between N_2 and O_4 (2.473 Å). That is, it might seem that there is an attractive interaction between the atoms X_2 and Y_3. Moreover, in molecule (**4**), the distance between O_2 and O_3 is longer than the O–O single covalent bond in hydrogen peroxide, 1.631 and 1.460 Å, respectively. Similarly the interatomic distance between N_2 and O_3 in molecule (**5**) is longer than a conventional N–O single covalent bond as in hydroxylamine, 1.635 and 1.448 Å, respectively. Figure 1 shows clearly that in molecules (**4**) and (**5**) there is not a BCP and BP for every pair X_2–Y_3. Therefore, according to Bader theory, there is not a bonding interaction between these atoms [33]. Very different is the situation in the corresponding acyclic species hydrogen peroxide and hydroxylamine, respectively. The calculations of local topological properties at the O–O BCP of the hydrogen peroxide [$\rho(\mathbf{r}_b) = 0.2779$ au, $\nabla^2\rho(\mathbf{r}_b) = -0.0558$ au and $H(\mathbf{r}_b) = -0.1939$ au] and at the N–O BCP of the hydroxylamine [$\rho(\mathbf{r}_b) = 0.2838$ au, $\nabla^2\rho(\mathbf{r}_b) = -0.3238$ au and $H(\mathbf{r}_b) = -0.2298$ au] present the typical characteristics of shared-shell interactions.

The C_1–O_2 bond in molecule (**4**) presents similar characteristics to a C–O single covalent bond as in methyl acetate [i.e., $d_{C–O} = 1.353$ Å, $\rho(\mathbf{r}_b) = 0.3065$ au, $\nabla^2\rho(\mathbf{r}_b) = -0.6532$ au and $H(\mathbf{r}_b) = -0.5027$ au].

In molecule (**5**), the C_1–N_2 bond is weaker than C–N partial double bond in methylacetamide [i.e., $d_{C–N} = 1.361$ Å, $\rho(\mathbf{r}_b) = 0.3325$ au, $\nabla^2\rho(\mathbf{r}_b) = -1.2202$ au and $H(\mathbf{r}_b) = -0.5247$ au], while the C_1–O_3 bond, as in the molecule (**4**), presents similar characteristic to a C–O single covalent bond as in methyl acetate.

The C_2–C_3 interatomic distance in (**6**) is longer than that of the C(sp^2)–C(sp^3) bond in its acyclic counterpart, the α-dicarbonyl, propane-1,2-dione ($d = 1.509$ Å). In addition, the topological properties $\rho(\mathbf{r}_b)$, $\nabla^2\rho(\mathbf{r}_b)$ and $H(\mathbf{r}_b)$ are lower in magnitude than the C(sp^2)–C(sp^3) bond in propane-1,2-dione [i.e., $\rho(\mathbf{r}_b) = 0.2532$ au, $\nabla^2\rho(\mathbf{r}_b) = -0.5816$ au and $H(\mathbf{r}_b) = -0.2115$ au]. That is, the C_2–C_3 bond in molecule (**6**) is slightly weaker than a conventional C–C single covalent bond.

A similar analysis shows that the O_2–C_3 bond in (**8**) is weaker than the unstrained C–O bond in propene-2-ol.

On the other hand, the ellipticity provides a measure not only for the π character of a bond but also its structural stability. Substantial bond ellipticities reflect structural instability, that is, the bond can easily be ruptured [29–31, 34]. Another criterion for structural stability is the distance between a BCP and a ring critical point (RCP). If these two critical points coalesce, they annihilate corresponding to bond rupture and concomitant ring opening. In molecules (**1**), (**2**) and (**3**), the X_2–Y_3 bonds have relatively large ε (0.67, 2.03 and 4.61, respectively) compared to unstrained species (e.g., ε = 0.01 for C–C bond in cyclohexane). In addition, in all these molecules, the RCP is closer to the X_2–Y_3 BCP than to the C_1–X_2 and C_1–Y_3 BCPs (see Fig. 1). These results allow us to establish that the X_2–Y_3 bonds in molecules (**1**), (**2**) and (**3**) are quite unstable.

Conclusion

In this work, a systematic theoretical study, within the QTAIM framework, was carried out to provide a description of the strength of the C_1–O_4, C_1–X_2, C_1–Y_3 and X_2–Y_3 bonds of the cyclopropanone derivatives: aziridine-2-one (**1**); oxirane-2-one (**2**); 1,2-diaziridine-3-one (**3**); 1,2-dioxirane-3-one (**4**); 1,2-oxaziridine-3-one (**5**); cyclopropane-1,2-dione (**6**); aziridine-2,3-dione (**7**); and oxirane-2,3-dione (**8**). The results of this theoretical study allow us to establish the following conclusions.

1. All interatomic interactions C_1–O_4, C_1–X_2, and C_1–Y_3 present typical characteristics of shared-shell interactions (covalent bonding). The X_2–Y_3 bonds are shared-shell interaction in (**1**), (**6**), (**7**) and (**8**) molecules, while in molecules (**2**) and (**3**), interactions within the closed-shell regime are observed. Between the atoms O_2 and O_3 in (**4**) and the atoms N_2 and O_3 in (**5**), there is not a bonded interaction.
2. The N_2–C_3, O_2–C_3, N_2–N_3, C_2–C_3 and O_2–C_3 bonds in molecules (**1**), (**2**), (**3**), (**6**) and (**8**), respectively, may be considered as weak single covalent bonds, while the N_2–C_3 bond in molecule (**7**) has some double-bond character.
3. The C_1–O_4 bond, in all molecules, is stronger than a conventional C–O double bond. The QTAIM bond order for the C_1–O_4 bond ranges from 2.07 in (**6**) to 2.39 in (**4**). In addition, a good linear correlation was found between the bond strength (measured through the bond order) and vibrational frequencies of the C_1–O_4 bond.
4. In general, the C_1–N bonds are rather much stronger than the C–N conventional single covalent bonds. In contrast, C_1–O bonds are only slightly stronger than C–O conventional single covalent bonds.
5. The C_1–C_3 bond in molecules (**1**), (**2**), (**6**) and (**7**) is slightly weaker than a conventional C–C single covalent bond.

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