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Bis-aniline compounds as potential candidates for molecular electronics: experimental and DFT investigation on 4,4'- diaminodiphenyloxide

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In this work, we present a joint experimental and theoretical investigation of bis-aniline derivative 4,4'-diaminodiphenyloxide (**dadpo**). This compound was proved as a building unit in designing supramolecular structures and as a precursor for the implementation of controlled molecular wires, suitable for inclusion in nanoscale information processing circuits. Different possible conformers, the optimum geometrical parameters and experimental vibrational and NMR spectra of this compound are obtained and assigned based on Density Functional Theory calculations performed by using B3LYP and BLYP exchange-correlation functionals, in conjunction with 6-31G(d) and cc-pVDZ basis sets. The lowest unoccupied molecular orbitals of the molecule are analyzed and discussed as possible paths for electron transport. It is found that the major conducting channels correspond to the LUMO+2 and LUMO+3 orbitals extended along the entire molecule. The influence of an external electric field on the shapes and energies of HOMO and LUMO orbitals, as well as on the HOMO-LUMO gap is also investigated.

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Keywords: Molecular wires, Bisaniline, FT-IR, Raman, NMR, DFT, HOMO, LUMO

1. Introduction

Poly-amino aromatic derivatives may be used as building units in the construction of channel-type supramolecular structures revealing catalytic and separation properties, due to their ability to generate N-H···E (E = N, O, S) intermolecular interactions [1,2].

Most important, quite recently, it was shown that aniline based compounds can play a very important role in designing organic materials for molecular electronics [3-5].

While the 4,4'-diaminodiphenylmethane (dadpm) is proved as an interesting precursor for the synthesis of two terminal molecular wires with a tunnel barrier [6,7,37], to the best of our knowledge, the similar 4,4'-diaminodiphenyloxide (**dadpo**) compound has never been considered for this kind of applications.

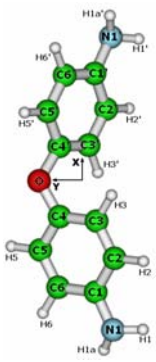

Fig. 1. Molecular structure of dadpo.

The aim of this work is to characterize the 4,4'-diaminodiphenyloxide molecule (Fig.1) by vibrational and NMR spectroscopies in conjunction with Density Functional Theory (DFT) calculations, in order to establish its structure and electronic properties. Thus, the experimental vibrational and NMR spectra of the title compound were assigned based on calculations performed at B3LYP and BLYP levels of theory with different basis sets.

In addition, the frontier molecular orbitals and the HOMO-LUMO gap of **dadpo** are calculated at B3LYP/6-31G(d) and TDDFT(B3LYP/6-31G(d)) levels of theory in order to estimate the potential barrier for electronic conduction of this compound and to compare the current results with those corresponding to methylene bridged aminophenyls [37].

2. Experimental

4,4'-diaminodiphenyloxide was purchased from a standard commercial source and used without further purification. FT-IR spectra of **dadpo** powder samples were recorded at room temperature on a conventional Equinox 55 FT-IR spectrometer by using KBr (Merck UVASOL) tablet samples. FT-Raman spectra were recorded in a backscattering geometry with a Bruker FRA 106/S Raman accessory equipped with a nitrogen cooled Ge detector. The 1064 nm Nd:YAg laser was used as excitation source, and the laser power was set to 400 mW. All spectra were

recorded with a resolution of 4 cm^{-1} by co-adding 32 scans.

The ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker AVANCE NMR spectrometer (400.13 MHz for ^{1}H and 100.63 MHz for ^{13}C, internal standard TMS), at the National Center of Magnetic Resonance, Babeş-Bolyai University, Cluj-Napoca.
The samples were prepared by solving **dadpo** in DMSO (signal for ^{1}H at 2.51ppm and at 39.5 ppm for ^{13}C). The spectra were recorded using a single excitation pulse of 12 μs for ^{1}H and 9 μs for ^{13}C. The FID signal was acquired 100 times for ^{1}H and 400 times for ^{13}C. [^{1}H,^{1}H] COSY NMR spectrum of **dadpo** in DMSO solution has been recorded by using a standard COSY45 d_1-π/2-d_2-π/4 pulse sequence.

3. Computational details

The molecular geometry optimizations, vibrational frequencies and NMR chemical shifts calculations were performed with the Gaussian 98W software package [8] by using DFT approaches, with B3LYP and BLYP [9,10] exchange functionals. The split-valence 6-31G(d) basis set of the Pople's group [11] has been generally used for the expansion of molecular orbitals. The correlation consistent cc-pVDZ basis set [12] was also used with B3LYP method, in order to calculate the NMR spectrum of the investigated molecule since this basis set was shown to perform much better than the standard 6-31G(d) basis set for calculating the ^{13}C chemical shifts [20].

The calculation of NMR spectra of **dadpo** was performed using the GIAO (Gauge-Including Atomic Orbitals) method [13], with the hybrid B3LYP exchange-correlation functional, in conjunction with 6-31G(d) and cc-pVDZ basis sets.

4. Results and discussion

4.1 Molecular structure of dadpo

Molecular structure, atom numbering scheme and axis system (OZ is perpendicular to the paper plane) for 4,4'-diamino -diphenyloxide molecule are given in Fig.1.

We optimized the structure of different conformers of **dadpo**, which differ in the relative orientations of the two amino groups with respect to the aromatic rings. The optimizations have been performed by using B3LYP and BLYP DFT methods, in conjunction with the 6-31G(d) and cc-pVDZ basis sets. The maximum relative energy between these conformers is less than 0.2Kcal/mol, a value which suggests that we can expect a mixture of all possible conformers in gas or liquid phase and also a large degree of freedom for NH_2 groups. All the methods used in calculations provide geometries with an almost C_2 symmetry showing a pyramidal structure for the two amino groups.

Experimental vibrational spectra of **dadpo** in solid state are given in Fig.2 and selected experimental and theoretical wavenumbers are collected in Table 1, along with the proper assignments.

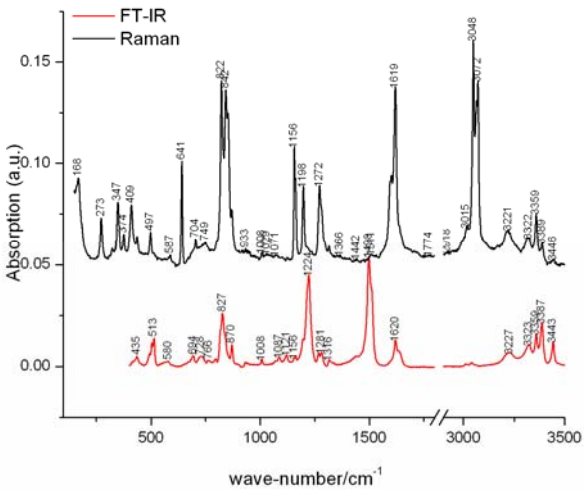

Fig. 2. Vibrational FT-IR (bottom) andFT- Raman (top) spectra of 4,4'-diaminodiphenyloxide.

To aid in mode assignments, we based on the direct comparison between experimental and calculated spectra by considering both the frequency sequence and the intensity pattern and by comparisons with other reported studies on similar compounds [14-23].

As seen in Table 1, the highest discrepancies between the experimental and theoretical wave-numbers are observed for the normal modes corresponding to vibrations related to the NH_2 group. Due to the tremendous importance of the amino group in directing the crystal lattice architecture, we consider the reliable assignment of its vibrations of maximum importance.

As compared to experimental data, the calculated values of these frequencies are predicted significantly larger both by B3LYP and BLYP methods. The significant disagreement between experiment and theory for these two modes is clearly due to the anharmonic effects, which for NH stretches are too important to be absorbed entirely in a simple scaling procedure, but also to the intermolecular interactions in which these molecules are involved in solid state [2,20,21].
As seen in Fig.2, FT-IR experimental spectrum shows a band at 3443cm^{-1} which clearly corresponds to the "free" (not involved in hydrogen bonding) NH_2 group. According to calculations, this band is due to the $\upsilon_{as}(NH_2)$ vibrations.

Table 1. Selected experimental and theoretical wave-numbers for 4,4'-diaminodiphenyloxide.

Mode	Experimental (cm^{-1})		Calculated (cm^{-1})*		Assignments**
	IR	Raman	B3LYP/ 6-31G(d)	BLYP/ 6-31G(d)	
1		168	160	154	γ(CN)
2		347	342	329	τ(rings)
3	435	435	432	417	ρ(rings)
4	493	497	501	485	γ(CH)+γ(CN)
5		587	591	572	δ(COC)+γ(CH) ring
6		641	645	629	ω(NH_2)
7	694	704	711	683	τ(rings)
8		842	847	811	γ(CH)
9	870	870	892	859	δ(CCC)
10	1156	1156	1147	1156	δ(CH)
11	1268	1272	1271	1273	ν(CN)+ν_{as}(CO C)
12	1281	1282	1275	1294	δ(CH)+ν(CC)
13	1316	1315	1319	1345	ν(CC)+ρ(NH_2) +δ(CH)
14	1510	1507	1506	1511	ν(CN)+δ(CH)
15		1600	1614	1614	ν(CC)+δ(NH_2)
16	1620	1619	1632	1649	δ(NH_2)
17	3040	3048	3054	3089	ν(CH)
18		3065	3090	3128	ν(CH)
19	3323	3316	3402	3417	ν_s(NH_2)
20	3359	3359	3403	3418	ν_s(NH_2)
21	3387	3389	3495	3512	ν_{as}(NH_2)
22	3443	3442	3497	3512	ν_{as}(NH_2)

* Scaled values [24]

** ν-stretching, δ-in-plane bending, γ-out-of-plane bending, τ-twisting, ω-wagging, ρ-rocking

The bands at 3359 and 3323cm^{-1} in the FT-IR spectrum of **dadpo** are assigned to the $\upsilon_s(NH_2)$ vibration. These bands are less intense than those corresponding to the asymmetric stretch vibrations and they are in good position and intensity pattern agreement with the experimental data for the solution of 4,4'-diaminodiphenylmethane (dadpm) in the hexane solvent [36]. In solid state, the bands corresponding to the $\upsilon_{as}(NH_2)$ vibrations of **dadpo** have been measured at 3443 and 3387 cm^{-1}, in good agreement with dadpm [37]. The same is true for the $\upsilon_s(NH_2)$ vibrations (see Table 6 in Ref.[36]). Our results prove that the symmetric stretching vibrations of NH_2 group are more affected by intermolecular interactions than the asymmetric stretching vibrations.

Another experimental evidence that support the intermolecular interactions is the existence of the broad band at 3227cm^{-1} and 3221 cm^{-1} in the FT-IR and Raman spectra, respectively. It is well known that the amino group of aniline can act in hydrogen bonds either as an H-atom donor or an H-atom acceptor [19]. Therefore, this rather weak and broad band is attributed to such NH...N intermolecular interactions. On the other hand, stronger NH...O intermolecular interactions are not excluded and their contributions to the broadening of this band can be also assumed. Based on the present and other studies performed in our group [20, 23, 37] by a standard fitting procedure we deduced a scaling factor of 0.9478 for the stretching vibrations of the NH_2 group, which leads to a very good agreement between the experimental and theoretical data.

Excluding the XH (X=C,N) stretching vibrations, the maxim deviations between the experimental (Raman) and theoretical data are 22 cm^{-1} and 31 cm^{-1} for B3LYP and BLYP calculated values, respectively. The standard deviations corresponding to the two methods are 8 cm^{-1} and 15 cm^{-1}. The maxim deviations are noted for the trigonal CCC bending in the case of B3LYP method and for the out-of-plane CH bendings for the BLYP functional. Even if BLYP combination is considered as reliable method for computing vibrational spectra, our results show that it is only superior to B3LYP hybrid functional for few exceptions, namely the in plan CH bendings and the trigonal CCC bendings (see Table 1).

Concluding, the very good agreement between theory and experiment allows us to confidently assign the vibrational spectrum of this molecule.

For a reliable assignment of NMR spectra of **dadpo**, our ^1H and ^{13}C NMR experimental investigation is coupled with DFT calculations. For NMR calculations purposes we

used the GIAO (Gauge-Including Atomic Orbitals) ansatz [13], implemented in the Gaussian package and the hybrid B3LYP functional, in conjunction with 6-31G(d) and cc-pVDZ basis sets.

Table 2. Experimental and calculated NMR chemical shifts of 4,4'-diaminodiphenyloxide molecule.

Nucleus	Experimental	Calculated	
		6-31G(d)	cc-pVDZ
C1, C1'	143.7	133.8	140.8
C2, C2'	115.0	107.8	112.6
C6, C6'		108.1	112.8
C3, C3',	119.0	113.0	117.3
C5, C5'		115.4	119.8
C4, C4'	148.6	142.9	149.7
H2, H2'	6.63	6.13	6.11
H6, H6'		6.21	6.24
H3, H3'	6.75	6.37	6.30
H5, H5'		6.70	6.71
H1, H1'	4.72	2.27	2.35
H1a, H1a'		2.31	2.38

The experimental and theoretical chemical shifts for **dadpo** are collected in Table 2. As seen in this table, the predicted ^{13}C chemical shifts depend drastically on the basis set used in calculations. Thus, the correlation consistent basis set provides significantly better computed values than the standard 6-31G(d) basis set. This fact can be related to a better description of the 1s and 2s core orbitals of the heavy atoms, which are expressed as a combination of 8 GTO, and also by including polarization functions on hydrogen atoms.

Excepting the amino protons, the ^{1}H chemical shifts are predicted in very good agreement with experiment. The calculated values for these protons are significantly smaller than the experimental counterparts and this suggests again intermolecular interactions occurring *via* NH_2 groups [20]. Moreover, the amino protons in dadpo are significantly deshielded with respect to dadpm and this fact can be corroborated with stronger NH...O intermolecular hydrogen bond interactions.

The bidimensional COSY ^{1}H–^{1}H NMR spectrum does not show off-diagonal peaks between the signals due to the protons in the NH_2 group and the ring protons. Thus, the NH…π intermolecular interactions which have been evidenced for dadpm, are either excluded or significantly less important for **dadpo**.

4.2 Dadpo as molecular wire

Both theoretically and experimentally, in order to make metal-molecule-metal junctions and thus to connect the molecules to the electrodes, S-functionalized molecules are usually synthesized [25,26]. However, in a very recent study [27] it was shown that the variability of the measured conductance for diamine molecule-gold junctions is much less than the variability for dithiol-gold junctions. This is due to the greater ability of the amines to bond to metal surfaces as two-electron donors, the bonding between gold and amines being a simple delocalization of the lone-pair electrons from the amine nitrogen to the surface gold atoms.

For these reasons we become interested in molecular system containing amino groups, which could function as molecular wires, and dadpm was shown as a potential precursor used for synthesis of molecular wires with a tunnel barrier [3, 37]. However, another possibility to interconnect the two aminophenyl rings is by joining them by an oxygen atom (i.e. **dadpo** molecule).

The stability and conduction properties of the molecular wires may be affected by the interaction and possible charge transfer between molecules. In order to avoid these effects, the encapsulation of molecules in nanotubes or cyclodextrines was proposed [28]. For estimating the influence of encapsulation on the HOMO-LUMO gap (HLG) for **dadpo**, the geometry of this molecule was optimized leaving free all the geometrical parameters and also freezing the dihedral angle between the two aromatic rings in order to keep them coplanar. Geometry optimization with this constrain provides a planar skeleton of the molecule which is expected to be similar to that corresponding to an encapsulated molecule in a cyclodextrine or carbon nanotube.

According to our calculations, both the HOMO and LUMO orbitals are destabilized for the planar molecule with respect to the non-planar structure and the LUMO is much more delocalized over the entire molecule, including the oxygen atom. However, the HLG is not significantly affected, its value being reduced from 4.84eV for non-planar structure to 4.62eV for a planar skeleton of the

molecule. This result shows that electronic transport properties will not be affected in a significant manner by including the molecule in an isolating environment.

The essential requirement for a molecule to behave as a molecular wire is to have a fully delocalized low lying unoccupied MO spreading all over the molecule and thus serving as conduction channel in the electron transfer process [29,30].

On the left side of Fig.3 are given the shapes of the first five LUMOs in the absence of the electric field, while on the right side the same orbitals are plotted in the presence of an applied electric field of 0.51V/Å. Their energies calculated at B3LYP/6-31G(d) level of theory are -0.04eV, 0.30eV, 0.55V, 0.95eV and 2.16eV without electric field and -0.83eV, -0.28eV, 0.32eV, 1.09eV and 1.57eV when the electric field is present. As easily can be seen, when no electric field is applied, the LUMO+2 and LUMO+3 orbitals are delocalized over the entire molecule, including the oxygen atom and amino groups. LUMO and LUMO+1 have almost the same shape, being not delocalized over the O atom and NH_2 group but only over the aromatic rings.

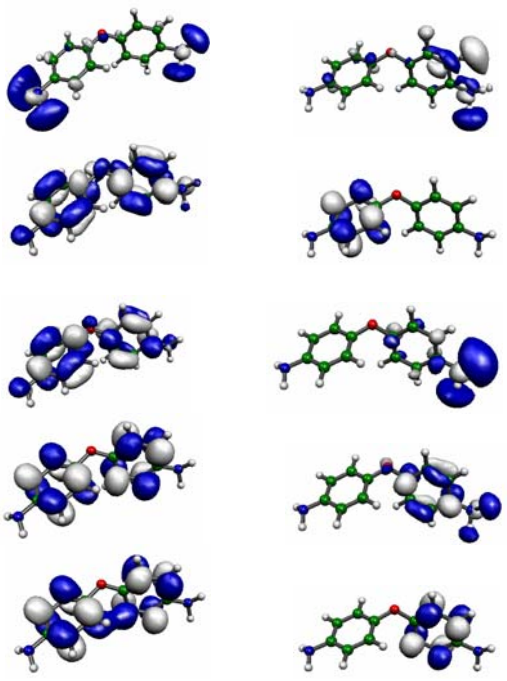

*Fig. 3. Orbital spatial orientation of five unoccupied molecular orbitals for **dadpo** plotted at 0.02a.u. electron density surface; a) without any external electric field; b) with an applied electric field of 0.51V/Å, parallel to OX axis (see Fig.1). From bottom to top: LUMO, LUMO+n, n=1, 2, 3, 4.*

On the other hand, the LUMO+4 is a MO mainly localized on the amino groups. Clearly, this MO cannot represent a conducting channel in this molecule but it could become very important if this amino group should be used as an "alligator clip" to a metal surface, i.e., when the molecule should be connected to the electrodes.

To promote a current across a molecular wire the relative energies of electronic levels of the molecule must be modulated by application of a voltage in order to generate a resonant tunneling process across the tunnel barriers [31]. Consequently, there is great interest in describing the evolution of the electronic structure of the wire as a function of a static electric field. In this respect, the LUMO plays a key role for the transport properties since the electrons begin to tunnel resonantly through the molecule when the LUMO is aligned to the Fermi level of the electrodes [31,32]. Based on this idea, the electric current through the molecule can be controlled by shifting specific molecular energy levels by the electric field.

The applied voltage required to bring the molecule to behave as a conductor is called the potential barrier for conduction and it is defined by [33]:

$$PB = \frac{1}{2} HLG + \Delta E_{LUMO} \quad (1)$$

where:

$$\Delta E_{LUMO} = E_{LUMO+n} - E_{LUMO} \quad (2)$$

LUMO+n being the conduction channel.

Thus, the estimation of this potential barrier implies the knowing of the HLG.

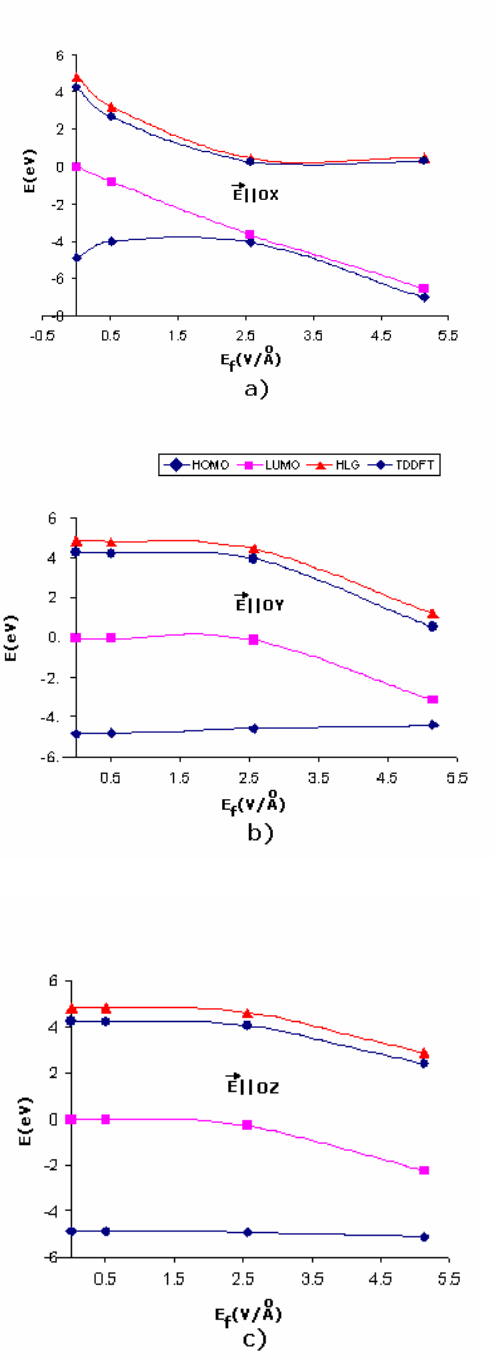

*Fig.4. Variations of HOMO and LUMO energies and HOMO-LUMO gap of **dadpo** as a function of applied electric field parallel to OX (a), OY (b) and OZ (c) axes. The orientation of the axis system is given in Fig.1.*

Using the B3LYP/6-31G(d) method we calculated the molecular energy levels and the HLGs of **dadpo** under the influence of an applied electric field and these dependencies are plotted in Fig. 4. It can be seen that HLG drops suddenly when the applied field is parallel to X axis, even for very small values of the field strength. On the other hand, significantly larger values of the field strength are necessary to obtain a similar drop of the HLG when

the field is parallel to the other two axes OY and OZ. The threshold of the electric field in the last two cases is about 2.5V/Å. Using eq. (1) and assuming LUMO as conduction channel, the potential barrier of **dadpo** for the case of $\vec{E}$ ||OX is 2.40eV as provided by DFT method and 2.10eV by TDDFT approach.

As seen in Fig.4, the HLG reduction upon the applied field is essentially due to the lowering of the LUMO's energy. Interestingly, a weak increase in the HOMO energy is observed for small values of the field strength when it is applied along the OX axis. When the electric field vector is parallel to OY and OZ axes no significant change in the energies of HOMO and LUMO are observed.

Hence, changes in the strength of the electric field can lead to changes in molecular energy levels, and thus, the conductivity of the molecule can be manipulated by varying the strength or direction of the applied field.

The HLGs obtained by DFT calculations are usually overestimated. However, the recent developed time dependent DFT technique [34,35] has proved to be a very useful tool for calculating the excitation energies and thus, for estimating the HLGs.

In order to obtain more accurate HLG values, the excitation energies of **dadpo** were calculated by TDDFT(B3LYP/6-31G(d)) method on the ground state optimized geometry at B3LYP/6-31G(d) level of theory.

The same trend of the HLG is obtained irrespective of the electric field direction. When no electric field is applied, the TDDFT method provides a correction of about 0.6eV for the HOMO-LUMO gap, the calculated value in this case being 4.24eV. This correction become significantly smaller as the electric field strength is increased.

5. Conclusions

Both, experimental and theoretical vibrational and NMR data, strongly suggest that the amino groups of this molecule intermediate intermolecular interactions of NH···N, NH···π, and NH...O type.

The overall very good agreement between the experimental and calculated vibrational and NMR spectra of this molecule allow us to confirm its structure.

In the absence of an external electric field the LUMO+2 and LUMO+3 orbitals represent the possible conduction channels in the electron transfer process, while LUMO+4 which is localized on the terminal NH_2 groups could play an important role when **dadpo** is connected to metal electrodes.

HOMO-LUMO gaps drastically depend on the orientation of the external electric field with respect to the molecular axis system. A dramatic lowering of LUMO is estimated for very low values of the electric field strength when it is applied along OX axis and a potential barrier of 2.10eV is estimated for **dadpo** in this case.

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